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JOURNAL
OF THE
AMERICAN CERAMIC SOCIETY

A monthly journal devoted to the arts and sciences related to the silicate industries.

Vol. 1 **November, 1918** **No. 11**

EDITORIALS.

GROWTH OF THE SOCIETY.

The American Ceramic Society has been in existence twenty years. During that time it has grown in membership from 22 to nearly 1100. The Society represents industries, the value of whose output—including clay products, glass and cement—aggregates $450,000,000 annually in the United States. The Society seeks to occupy towards the clay, glass and cement industries the same position of leadership that the American Chemical Society, the American Society of Civil Engineers, the American Society of Mechanical Engineers, the American Institute of Mining Engineers, and some others, occupy in their respective fields. The 100 per cent increase in membership of the Society during the past two years indicates the need of an organization of its kind and augurs well for the future welfare and growth of the Society.

The Society should, however, profit by the experience and example of other technical organizations and endeavor to coordinate its activities through permanent officials, having no other business in life than the advancement of the Society's interests. With the steady growth in membership and the widening and intensification of its activities through the Journal, Local Sections, Professional Divisions, etc., the Society's business is becoming too large and varied to depend upon the part time services of its committees and executive officers. With the in-

creased revenue through the accession of new members and the gratifying support from firms and corporations through contributing memberships, the time is fast approaching when the Society will be fully able to financially support the coördination of its activities through full-time executive officers. Let us lend our efforts in this direction!

KILNS.

There is no problem of more importance facing the manufacturer of ceramic products than that of the selection of the type of kiln best suited for the burning of his wares. The low efficiency of the average periodic kiln renders it the greatest source of economic loss in most of the plants where used. The rising cost of fuel and the necessity of its conservation in the future render the kiln question an increasingly vital one.

The discussions in recent numbers of this and other Journals as to the efficiencies and applicability of the available types of kilns to the burning of the different kinds of ceramic products leave the selection in most cases a wide open one, and a verdict has not as yet been reached. The question recently raised in the editorial columns of a contemporary Journal as to the design and efficiency of the modern by-product coke ovens should give ceramic engineers and manufacturers serious food for reflection. Have we arrived at the millennium in kilns or will the future produce radical types far superior to any which have been placed upon the market thus far? It is doubtless true that no one type of kiln will be developed which will be applicable to the burning of all grades of ceramic wares.

The suggestion that at the next annual meeting of the Society there be a symposium on kilns should receive attention at once. At that time the presentation of reliable data as to the relative efficiencies of the different types of kilns now in use and also unbiased reports as to the service rendered will be a step forward in the solution of this vexing problem. In the meantime, there is need for more data as to the efficiencies of present installations, and it is to be hoped that ceramic engineers will continue to collect and make data of this kind available.

ORIGINAL PAPERS AND DISCUSSIONS.

A CONTRIBUTION TO THE METHODS OF GLASS ANALYSIS, WITH SPECIAL REFERENCE TO BORIC ACID AND THE TWO OXIDES OF ARSENIC.

By E. T. Allen and E. G. Zies.

In the course of the work on optical glass undertaken by the Geophysical Laboratory in the year 1917–18 some investigation was made of the well-known Jena optical glasses. It included among other things complete chemical analyses of a considerable number of them, to determine the composition in doubtful cases and to see if anything could be learned respecting the relation of composition to quality. In this connection the authors spent considerable time in testing the accuracy of certain analytical methods and in devising others, an account of which is here given.

We had supposed that the system of silicate analysis so well worked out for rocks by Hillebrand and others could be applied with little or no change to glasses. But glasses contain certain elements like boron and arsenic seldom found in rocks in appreciable quantities; many such elements, in fact, if all sorts of glass are considered. Again, glasses contain certain combinations of elements which are difficult to separate and determine accurately by ordinary methods. On the whole we have found them considerably more difficult to analyze than rocks.

E. C. Sullivan and W. C. Taylor have realized these difficulties and have made valuable contributions to the subject,[1] especially along the line of rapid analytical methods. Our work may supplement theirs in some measure. We have devoted our attention

[1] *J. Ind. Eng. Chem.*, **6**, 897 (1914).

for the most part to optical glasses, and our chief purpose has been to improve the accuracy of the methods. At the same time in the work done on boric acid and the two oxides of arsenic we have also kept in mind the more general utility of the methods.

I. Determination of Trivalent and Pentavalent Arsenic.

It may be confessed at the outset that the time and space devoted in this paper to the determination of arsenic will probably seem entirely disproportionate to the rest of the subject. The chief reason for the more detailed study of this determination was our interest in the role which arsenic plays in glass making. The percentage of arsenic in glasses is so small that if we are to follow successfully its history from the batch to the finished glass we must have an unusually accurate method for its determination. When later it became evident from our work that Gooch and Browning's very accurate iodometric method for arsenic acid could be applied to the determination of arsenic in all substances where it could first be accurately transformed into the sulphide, we felt further justified in the course we had followed.

Glass commonly, but not invariably, contains arsenic. All the Jena optical glasses which we have examined contain it. The total arsenic in glass may be directly determined by fusing a weighed portion with alkali carbonate and nitrate, removing any nitric acid which remains by evaporating to dryness with sulphuric acid, filtering off the silica and insoluble sulphate, if any, and precipitating the arsenic as sulphide; this may finally be transformed into magnesium pyroarsenate and weighed, or reduced by hydriodic acid and titrated with standard iodine solution.

When a mixture of arsenic acid and arsenious acid is evaporated in platinum with hydrofluoric and sulphuric acids, the arsenious acid is completely volatilized as the trifluoride, while all the arsenic acid remains in the residue entirely unreduced. Thus the two oxides are very accurately separated from one another; the pentavalent arsenic may be determined in the residue and the trivalent arsenic by difference between the pentavalent and total arsenic. The trivalent arsenic can also be *directly* determined in the distillate if the operation is carried out in a gold or platinum still of suitable form.

1. **Determination of Total Arsenic.**—There is no element of originality in this determination; we have simply proved by synthetic experiments that no arsenic is lost in a fusion with sodium carbonate and niter, and that fairly satisfactory estimations of the total arsenic in glass may be made after separating the arsenic as sulphide, oxidizing the latter with hydrogen peroxide and ammonia, precipitating the arsenic from this solution as magnesium ammonium arsenate and finally weighing it as pyroarsenate. Further, if the solution formed by oxidation with hydrogen dioxide and ammonia is reduced by hydriodic acid and titrated by a standard iodine solution, after the method of Gooch and Browning, the determination becomes highly accurate and may be done in far less time.

Volatilization of Arsenic in the Process of Fusion Involved in Analysis.—Unfortunately for the purposes of analytical control it is not possible to prepare a glass which shall contain a given amount of arsenic trioxide and probably not possible to prepare one carrying a given amount of arsenic pentoxide. The possible loss of arsenic by volatilization during the fusion with sodium carbonate which is involved in the decomposition of a glass for analysis, had therefore to be tested indirectly. To this end we took mixtures of arsenious oxide in known quantity and a powdered glass containing no arsenic. To these were added 3 g. pure dry sodium carbonate per gram of glass, the fusion was made as in an ordinary determination of silica and the arsenic was determined in the product. An appreciable quantity of arsenic was lost.

Taken	0.0530 g. As_2O_3
Found 0.0797 g. $Mg_2As_2O_7$ equivalent to	0.0508 g. As_2O_3
Loss	0.0022 g. As_2O_3

In a second experiment:

Taken	0.0710 g. As_2C_3
Found 0.1058 g. $Mg_2As_2O_7$ equivalent to	0.0674 g. As_2C_3
Loss	0.0036 g. As_2O_3

When a small amount of niter, about 0.1 g., was added to the

flux a still greater quantity of arsenic trioxide was fused *without* loss.

Taken.....	0.1010 g. As_2O_3
Found 0.1589 g. $Mg_2As_2O_7$ equivalent to	0.1013 g. As_2O_3
.....	0.0003 g. As_2O_3

The determination of the arsenic was made as outlined above and described in detail further on. Now, although it is quite possible that *arsenic which is combined in a glass* might be entirely retained when the glass was fused with sodium carbonate *alone*, it is undoubtedly safer to add niter, for the carbonate sometimes contains bits of organic matter, possibly paper or cardboard, which would almost certainly lead to the volatilization of metallic arsenic during the fusion of the glass. Convenient details for the method follow:

Fuse 1 g. of powdered glass with 3 g. pure, dry sodium carbonate and about 0.1 g. potassium nitrate. When cool, set the crucible in a 12 cm. casserole, add water, cover and put in 10 cc. 1 : 1 sulphuric acid.[1] Warm until the fusion cake is removed, clean and remove the crucible and evaporate till white fumes appear. Heat somewhat longer until the silica becomes dense enough to filter without trouble; cool, add hot water and boil till any insoluble sulphate settles satisfactorily. Barium gives trouble here, because in evaporating to dryness the sulphate is partially redissolved in the concentrated sulphuric acid and is again precipitated in a fine state of division by the addition of water. Filter with suction, wash a few times with boiling water and *suck dry*. The filtrate may be kept down to 100 cc. For fear the bulky precipitate may retain a little arsenic, open the filter and transfer the precipitate to a 20 cc. platinum crucible with the aid of a stout platinum wire, add a little sulphuric acid and 5 cc. hydrofluoric acid and evaporate to white fumes. Cool, transfer the residue to a small beaker with a little hot water, boil and filter, adding the filtrate to the principal one. To the filtrate from silica add a fragment of potassium iodide, heat and

[1] Hydrochloric acid cannot be used here because, as is well known, arsenious acid is thus volatilized as the trichloride, and even arsenic acid is partially reduced and volatilized.

precipitate the arsenic with hydrogen sulphide. The precipitation is materially accelerated by the reduction of the arsenic acid by hydriodic acid. When the precipitate has well coagulated, cool partially in order that the solution may absorb some excess of hydrogen sulphide, stopper and set aside. If the solution is filtered immediately the results are likely to be too low.

Experiments were made on the precipitation of the arsenic from a strong hydrochloric acid solution, *without previous separation of silica*, but so much silica came down with the sulphide causing so much subsequent trouble that this method was abandoned.

Of course if antimony is present it will have to be separated from the arsenic by one of the regular methods. If the glass contains lead, the precipitate will generally have an orange color, but the color is due to the presence of a little sulphide of lead. If the sulphate solution is allowed to stand before treatment with hydrogen sulphide till the lead is completely precipitated the sulphide precipitate is a clear yellow. The addition of arsenic and antimony together has been tried in glass making, but all the glasses we have examined contained either one or the other but not both. After standing overnight, the arsenic sulphide is filtered and washed with hot water acidulated with sulphuric acid.

The sulphide is then treated on the filter with a few cc. of strong ammonium hydroxide, and the flask rinsed with the same. The filter is washed two or three times with a few cc. of hot water. If it shows any residue after the solution of the arsenic it is transferred to a 150 cc. beaker and digested warm with ammonia and a little ammonium carbonate. The orange precipitates mentioned above have to be digested a short time before they show the dark brown color of lead sulphide, and the suspicion is that till then they still retain arsenic. The soluble portion is added to the principal arsenic solution, which is conveniently handled in a 250 cc. beaker, and oxidized by hydrogen peroxide—3 to 5 cc. of a 3 per cent solution is sufficient. Cover the beaker and boil for some time on the hot plate to complete the oxidation and decompose the excess of peroxide. We have confirmed the statement in the textbooks that a complete oxidation is accomplished in this way

Levol's Method[1] **for the Determination of Arsenic.**—If the arsenic is to be determined gravimetrically, the solution is now precipitated with magnesia mixture, the precipitate is washed, dried at 130° and then slowly heated in the electric oven to 550° where it appears to be stable. The precipitate gains again on the balance (1 to 2 mg. in the case of a large precipitate), and the final weight agrees best with the quantity of arsenic taken, though this may be due to a compensation of errors. Our results by this method on pure arsenic solutions were satisfactory, as the sequel shows, but the results on glasses did not show the accuracy which our ultimate purpose required. (See p. 760.) It will be remembered that one cannot control his results by working with a synthetic glass containing a known quantity of arsenic; he must depend on the agreement of duplicate determinations and the comparison of different methods. The following table shows the agreement of results which one may obtain when the Levol method is applied to the determination of arsenic in glasses.

TABLE 1.

Total arsenic in some Jena optical glasses determined as $Mg_2As_2O_7$, showing the agreement of duplicates. Results in milligrams per gram of glass.

No.	1	2	3	4	5	6	8	9	11	15
Kind of glass. *Schott's numbers.	*O3832*	*O340*	*O154*	*O144*	*O167*	*O211*	*O2071*	*O1209*	*O722*	*O599*
$Mg_2As_2O_7$....	7.0	5.2	2.9	3.9	3.4	6.1	7.1	5.5	7.2	3.7
	5.8	6.5	2.7	4.0	3.6	7.2	8.3	6.2	8.1	4.1
Mean.....	6.4	5.8	2.8	4.0	3.5	6.6	7.7	5.8	7.7	3.9
Equivalent to As_2O_5.....	5.2	3.9	2.1	2.9	2.5	4.5	5.2	4.1	5.3	2.7
	4.3	4.8	2.0	3.0	2.7	5.3	6.2	4.6	6.0	3.0
Mean.....	4.8	4.3	2.0	3.0	2.6	4.9	5.7	4.4	5.7	2.9
Variation in As_2O_5.....	0.9	0.9	0.1	0.1	0.2	0.8	1.0	0.5	0.7	0.3

* See Doelter's "Handbuch der Mineralchemie," Bd. I, 6, pp. 871–889, for the approximate composition of some of these glasses.

[1] See especially Levol, *Ann. chim. phys.*, [3] **17**, 501; Austin, *Am. Jour. Sci.*, [4] **9**, 55 (1900).

The method may serve very satisfactorily for large quantities of arsenic, but for these small amounts the percentage error is inadmissibly high. As the Levol method is the handiest method for the determination of arsenic where only occasional results are required, we spent some time in the effort to increase its accuracy.

When the results in Table 1 are compared with those obtained later by the Gooch and Browning method (see Table 3) a number of them are found to be considerably too high. Several magnesium ammonium arsenate precipitates obtained in the analysis of glasses were examined for insoluble matter like silica, lead sulphate or barium sulphate, but solution in a few drops of warm dilute hydrochloric acid failed to reveal any. When the filter and residue were incinerated, never over 0.2 mg. was found.

The only possible clue to the high results which we have is one abnormally high determination obtained by precipitating magnesium ammonium arsenate in the presence of considerable hydrogen peroxide.

Taken.	Found.
As_2O_5... 0.0116 g.	$Mg_2As_2O_7$..... 0.0392 g.
H_2O_2... 5 cc. 3 per cent solution	As_2O_5..... 0.0290
Total volume about 25 cc.	

We do not know the meaning of this result, but if hydrogen peroxide can cause too high results in the precipitation of arsenic by magnesia mixture, some of our errors in the determination of arsenic by the Levol method may have been due to the incomplete removal of hydrogen peroxide from the solution after the oxidation of the arsenic.

Further work on this line was abandoned when we had tested the volumetric method described below.

Method of Gooch and Browning.—Much more accurate than the Levol method is the method of Gooch and Browning[1] according to which the arsenic acid is reduced by hydriodic acid to arsenious acid which is then titrated with a standard solution

[1] *Am. Jour. Sci.*, **3**, 40, 66 (1890).

of iodine in the usual way. Gooch and Browning worked only with pure solutions of arsenic acid, so that we were obliged to test the applicability of the method to solutions formed by the oxidation of arsenic sulphide with hydrogen peroxide and ammonia.

For these and subsequent tests we used a standard solution of arsenic acid made as follows: First a sample of arsenious oxide was selected from several in stock on the basis of microscopic examination. The sample selected was practically homogeneous showing no intermixture of a higher refracting substance suggestive of the presence of antimony, as some others did. For this examination the authors are indebted to Dr. H. E. Merwin whose experience in such work is quite exceptional. Solution of a portion of the sample in hydrochloric acid showed no residue of sulphide. This sample was sublimed at low temperature several times, only the first fraction in each sublimation being retained. The powdered product was then dried over calcium chloride. For some work it may be that a more rigorous criterion of purity would be required, but the experiments which follow show this preparation to have been quite pure enough for our purposes.

1.0003 g. of this preparation of As_2O_3 was put into a platinum dish and covered with a watch-glass. Concentrated nitric acid was added and evaporated on the water bath, the operation being once repeated. Finally the temperature was carried to about 200° on the electric hot plate and held there till the fumes of nitric acid could no longer be detected. The arsenic acid was dissolved and made up to 100 cc.

10 cc. of this solution was precipitated and determined as $Mg_2As_2O_7$.

Taken 0.1000 g. As_2O_3 equivalent to.....	0.1161 g. As_2O_5
Found 0.1569 g. $Mg_2As_2O_7$ equivalent to...	0.1161 g. As_2O_5

The solution was prepared and evaluated before the adoption of the Gooch and Browning method. For some of the tests another more dilute solution was made in the same way from the same sample of arsenic trioxide. Measured volumes of the standard solution of arsenic acid were diluted with water and made

decidedly acid, 5 cc. 1 : 1 H_2SO_4 to 100 cc. total volume, a little potassium iodide was added and the arsenic was precipitated by hydrogen sulphide. The washing and oxidation of the sulphide have already been described. When, in the course of the oxidation, the ammonia has been expelled and the solution has been reduced to 10 or 15 cc. by evaporation on the hot plate, about 7 cc. 1 : 1 H_2SO_4 is added and the boiling continued about fifteen minutes. Some oxidizing agent[1] formed by the hydrogen dioxide, doubtless a mixture of nitrite and nitrate, is thus removed. If sulphur or sulphide of arsenic is precipitated when the acid is added, the oxidation is of course incomplete. The Gooch and Browning method is carried out advantageously as follows: Pour the oxidized solution into a 300 cc. Erlenmeyer flask marked with a "glass" pencil at the levels to which 40 cc. and 100 cc. of liquid fill it. Dilute the solution to the 100 cc. mark with hot water and add a fragment of potassium iodide—0.3 g. is sufficient for small quantities of arsenic. The two-bulb trap used by Gooch and Browning is set into the neck of the flask, and the liberated iodine is expelled by vigorous boiling. A stream of carbon dioxide led in through a capillary tube prevents bumping and aids in driving out the iodine which the solution retains tenaciously. Gooch and Browning evaporate to 40 cc. and then remove the iodine which remains by rapid addition of very dilute sulphurous acid in required quantity. We regard it as a little more accurate to remove the iodine *entirely* by repeated boiling. To this end add another portion of water (25 cc.), also another fragment of potassium iodide to insure complete reduction, and boil down again to 40 cc., repeating the operation till the solution is colorless. Then dilute quickly with cold water to 75 or 100 cc. and complete the cooling by whirling the flask in a vessel of ice water. Pour in 12 to 14 cc. of a "saturated" solution of potassium carbonate, which has the advantage over sodium carbonate of greater solubility. This neutralizes the major part, but must not neutralize all, of the sulphuric acid. The neutralization is completed by solid sodium bicarbonate. Add starch paste and titrate. It is not well to cool the solution

[1] Ilosvay de Nagy Ilosva, *Ber.*, **28**, 2031 (1895); *Bull. Soc. Paris*, **3**, 2, 351 (1889).

below, say, about 20° or 25° since the speed of the reaction with iodine is then considerably retarded. We use a solution containing about 1.1 g. iodine per liter of solution, so that 1 g. of solution is equivalent to about 0.5 mg. As_2O_5. The standard solution is

TABLE 2.

Showing the accuracy of the arsenic determination by the iodometric method when the arsenic is first precipitated as sulphide, oxidized by H_2O_2, reduced, and titrated.

	1.	2.	3.	4.	5.
Grams iodine solution required	4.71[1]	7.85[1]	11.82[2]	23.30[2]	57.95[2]
Equivalent to mg. As_2O_5	2.1	3.5	5.8	11.5	28.6
Mg. As_2O_5 taken	2.3	3.5	5.8	11.6	29.0
Error	0.2	0.0	0.0	0.1	0.4

weighed in a weight burette.[3] The very satisfactory results in Table 2 show that the Gooch and Browning method for arsenic may be made general, or at any rate that it may be used in all cases where the arsenic can be previously transformed into the sulphide without loss.

The method was now applied to the determination of total arsenic in a series of glasses. The process was that described on page 742, except that the arsenic acid was reduced and titrated with iodine instead of being weighed as pyroarsenate of magnesium. The results appear in Table 3. In these 14 pairs of duplicate determinations, in each of which 1 g. of glass was used, the maximum variation is 0.3 mg. and the mean variation only 0.1 mg. The method is to be commended for its speed as well as its accuracy.

[1] 1 g. of this solution was equivalent to 0.000446 g. As_2O_5.

[2] 1 g. of this solution was equivalent to 0.000494 g. As_2O_5.

[3] For improvements in the iodometric metric method for arsenious acid, see E. W. Washburn, *J. Am. Chem. Soc.*, **30**, 31 (1908).

TABLE 3.

Total arsenic in glasses determined iodometrically, in duplicate. As_2O_5 in milligrams per gram of glass.[1]

No. of glass.	Kind of glass.	G. iodine solution used.	Mg. As_2O_5 found.	No. of glass.	Kind of glass.	G. iodine solution used.	Mg. As_2O_5 found.
1.....	Jena	7.12	3.2	9..	Jena	11.48	5.1
	O3832	7.14	3.2		O1209	11.58	5.1
2.....	Jena	6.34	2.8	11..	Jena	13.74	6.1
	O340	6.04	2.7		O722	14.25	6.3
4.....	Jena	6.58	2.9	13..	Jena	10.82	5.3
	O144	6.50	2.9		O578	10.03	5.0
5.....	Jena	7.24	3.2	15..	Jena	6.10	3.0
	O167	6.49	2.9		O599	6.17	3.0
6.....	Jena	7.60	3.4	20..	P. P. G. Co. Spectacle	21.71	10.7
	O211	7.05	3.1		P. P. G. Co. Crown	21.58	10.7
7.....	Jena	11.95	5.3	21..	P. P. G. Co. Green Plate	5.61	2.8
	O2122	11.94	5.3			5.62	2.8
8.....	Jena	13.20	5.9	22..	P. P. G. Co. Dense Flint	19.71	9.7
	O2071	13.32	5.9			19.56	9.7

The Separation of Trivalent from Pentavalent Arsenic[2] and the Determination of Each.—The separation of the two forms of arsenic can be accurately made by heating the mixture in platinum with hydrofluoric and sulphuric acids. The arsenious acid is changed into the trifluoride which is easily and completely volatilized, while *all* the arsenic acid remains in the residue. The operation is conveniently carried out by heating the material in a capacious and loosely covered platinum crucible or small dish by means of an electric hot plate to a final maximum temperature of about 200°. We used crucibles holding 40 or 60 cc. and raised the lid slightly by setting a piece of heavy platinum

[1] In determinations 1–11, inclusive, iodine sol. I was used; 1 g. solution equivalent to 0.000446 g. As_2O_5. In determinations 13–22, inclusive, iodine sol. III was used; 1 g. solution equivalent to 0.000494 g. As_2O_5.

[2] This separation has not been worked out for mixtures which contain antimony.

wire across the top of the crucible. Bumping was prevented by dropping a piece of crumpled platinum foil into the crucible along with the contents and evaporation was accelerated by surrounding the crucible by a fire-clay cylinder.

Standard solutions of arsenious and arsenic acids were used in this series of experiments. The preparation of the standard solution of arsenic acid has already been described (see p. 746). The arsenious solution was made by dissolving a weighed portion of As_2O_3 in a little warm caustic soda solution, diluting sufficiently and acidifying with dilute sulphuric acid. The solution was then cooled and made up to a given volume. 10 cc. arsenious solution containing 0.1000 g. Ag_2O_3 was mixed with 1–2 cc. 1 : 1 H_2SO_4 and 5 cc. HF and evaporated on the hot plate to white fumes. The residue was cooled, diluted with water, neutralized by sodium bicarbonate and tested with starch paste and dilute iodine solution; the first drop struck a blue color. The solution was now acidified with hydrochloric acid, made alkaline with ammonia and tested with magnesia mixture. No precipitate was obtained.

Again 10 cc. of the same arsenious solution was treated in the same way. This time the residue was dissolved in water and tested with hydrogen sulphide. No arsenic was found. All trivalent arsenic is therefore volatilized by heating a substance containing it with hydrofluoric acid in the manner described.

5 cc. of the *arsenic acid* containing 0.0585 g. As_2O_5 was now treated with sulphuric and hydrofluoric acids in a similar manner. The residue was dissolved in water and precipitated by magnesia mixture.

Taken	0.0585 g. As_2O_5
Found 0.0791 g. $Mg_2As_2O_7$ equivalent to	0.0581 g. As_2O_5
Error	0.0004 g. As_2O_5

This shows that arsenic acid is not reduced or volatilized by hydrofluoric and sulphuric acids.

When the pure arsenious solution is evaporated on the hot plate to white fumes (max. temp. about 200°) with *sulphuric acid alone* no arsenic is volatilized.

Taken	0.1000 g. As_2O_5
Found 0.1562 g. $Mg_2As_2O_7$ g. equivalent to	0.0995 g. As_2O_5
Error	0.0005 g. As_2O_5

In Table 4 (page 752), mixtures of the two standard solutions were used, and to test at the same time the validity of the method for glasses, 1 g. (or in determinations 6 and 7 for lack of material, 0.5 g.) of powdered glass free from arsenic was added to the mixture. In determinations 6 and 7 a flint glass containing 45 per cent lead oxide was used. These results, like those immediately preceding, were done before the method of Gooch and Browning was adopted; hence the arsenic was weighed as magnesium pyroarsenate. They show in a convincing way that the method suffices for an accurate separation of the two oxides of arsenic while the presence of powdered optical glass in no way interferes with it. Also the conditions under which the determinations are made so nearly simulate those of a determination of the arsenic in glass that one can hardly question that the method will suffice to determine the two forms of arsenic in a glass—at least an optical glass where substances which might possibly interfere with the process, such as iron and chlorine, are present in minimum quantity.

S. R. Scholes[1] believed he had determined both oxides of arsenic in glass, in the following way: A weighed portion of glass was dissolved in *hydrofluoric acid and then evaporated with sulphuric acid till the hydrofluoric acid was driven out.* In this solution he reduced the arsenic acid by hydriodic acid and titrated the liberated iodine in the acid solution with standard thiosulphate. He then made the solution alkaline with sodium bicarbonate and titrated the total arsenic with standard iodide. We now know that the solution he used could not have contained any of the arsenious oxide and that his small differences were only the variations between two methods in both of which the arsenic pentoxide and *only* that was actually determined.

Pentavalent Arsenic in Glass.—The above method of separating the two forms of arsenic was now applied to the glasses in

[1] *J. Ind. Eng. Chem.*, **4**, 16 (1912).

TABLE 4.

Showing the separation of given quantities of trivalent from pentavalent arsenic and the determination of the latter.[1]

	1.	2.	3.	4.	5.	6.	7.
	g.	g.	g.	g.	g.	g.	g.
As_2O_3 taken	0.0100	0.1000	0.0100	0.0500	0.0100	None	None
As_2O_5 taken	0.0023	0.0058	0.0116	0.0581	0.1161	0.0058	0.0035
$Mg_2As_2O_7$ found	0.0032	0.0075	0.0152	0.0777	0.1565	0.0069	0.0052
Equivalent to As_2O_5	0.0024	0.0055	0.0113	0.0575	0.1158	0.0051	0.0038
Variation from As_2O_5 taken	0.0001	0.0003	0.0003	0.0006	0.0003	0.0007	0.0003

Table 3 and the pentavalent arsenic was determined in each by the Gooch and Browning method. The results are recorded in Table 5. Duplicate determinations show a maximum variation of 0.3 mg. and a mean variation of 0.1 mg. just as in the determinations of total arsenic. In Table 6 are tabulated the amount of arsenic pentoxide in each glass, together with the amount of arsenic trioxide found by difference between the pentavalent and the total arsenic. Evidently the major part of the arsenic is in the form of pentoxide, indeed the trioxide is so small, ranging from zero to a maximum of 0.09 per cent of the glass, that one is inclined to suspect some systematic and tolerably constant error between the two methods. It seemed quite improbable that errors of this degree of constancy could be caused by spattering on the hot plate during the solution of the glass. Still some losses in the beginning of the work, when fewer precautions were taken, were traced to this source. Before going further, therefore, it was proved beyond question that the results were affected by no such errors.

Effect of the Presence of Ferrous Iron in the Separation of the Two Forms of Arsenic.—It occurred to us that the small differences found between the total and pentavalent arsenic in glasses might be due to the reducing action of ferrous iron. All glasses contain a small amount of iron some of which may be ferrous. Now if this should reduce a little of the pentavalent

[1] Determined as $Mg_2As_2O_7$.

TABLE 5.

Pentavalent arsenic in glasses determined iodometrically in duplicate. As_2O_5 in milligrams per gram of glass.[1]

No. of glass.	Kind of glass.	G. iodine solution used.	Mg. As_2O_5 found.	No. of glass.	Kind of glass.	G. iodine solution used.	Mg. As_2O_5 found.
1.....	Jena	4.72	2.1	9....	Jena	10.92	4.9
	*O*3832	5.06	2.3		*O*1209	10.74	4.8
2.....	Jena	6.23	2.8	11...	Jena	12.34	5.4
	*O*340	6.23	2.8		*O*722	12.55	5.6
4.....	Jena	4.82	2.1	13...	Jena	11.62	5.1
	*O*144	4.19	1.9		*O*578	11.34	5.0
5.....	Jena	5.38	2.4	15...	Jena	5.81	2.6
	*O*167	6.02	2.7		*O*599	5.93	2.6
6.....	Jena	5.78	2.6	20...	P. P. G. Co. Spectacle	19.94	9.9
	*O*211	5.92	2.6		Crown	19.78	9.8
7.....	Jena	10.18	4.5	21...	P. P. G. Co. Green Plate	3.69	1.8
	*O*2122	10.19	4.5			3.51	1.7
8.....	Jena	12.16	5.4	22...	P. P. G. Co. Dense Flint	18.37	9.1
	*O*2071	12.23	5.5			18.25	9.0

arsenic to the trivalent state during the solution of the glass by sulphuric and hydrofluoric acids, this trivalent arsenic would at the same time be volatilized and therefore the pentavalent arsenic would always be *found* lower than the total arsenic even when the arsenic was entirely in the pentavalent state. The following experiments were tried to test this point.

Known amounts of ferrous sulphate were introduced into the crucible along with measured quantities of arsenic acid and the evaporation with hydrofluoric and sulphuric acids made as before.[2]

[1] Determinations 1–9 inclusive were made with iodine sol. I; 1 g. sol. equiv. to 0.000446 g. As_2O_5. Determinations 11–15 inclusive were made with iodine sol. II; 1 g. sol. equiv. to 0.000442 g. As_2O_5. Determinations 20–22 inclusive were made with iodine sol. III; 1 g. sol. equiv. to 0.000494 g. As_2O_5.

[2] Here, as in some previous results, the work was done before the more accurate iodometric method was adopted.

TABLE 6.

Showing both trivalent and pentavalent arsenic in glass, determined iodometrically.[1]

Mg. per gram of glass.

Number of Glass.	1	2	4	5	6	7	8	9	11	13	15	20	21	22
												P. P. G. Co.		
Kind of Glass.	JENA.											Spectacle Crown	Green Plate	Dense Flint
	O3832	O340	O140	O167	O211	O2122	O2071	O1209	O722	O578	O599			
Grams iodine solution equivalent to total arsenic (mean)	7.13	6.19	6.54	6.86	7.32	11.95	13.26	11.53	14.00	10.42	6.13	21.65	5.61	19.63
Grams iodine solution equivalent to pentavalent arsenic (mean)	4.89	6.23	4.50	5.70	5.85	10.18	12.20	10.83	12.34	10.27	5.25	19.86	3.60	18.31
Difference	2.24	0.04	2.04	1.16	1.47	1.77	1.06	0.70	1.66	0.15	0.88	1.79	2.01	1.32
As_2O_3 in mg., equiv. to difference	0.9	..	0.8	0.4	0.6	0.7	0.4	0.3	0.7	0.1	0.4	0.8	0.9	0.6
Mg. As_2O_5 directly determined (mean)	2.2	2.8	2.0	2.5	2.6	4.5	5.5	4.9	5.5	5.1	2.6	9.9	1.8	9.1

[1] Determinations 1–9 inclusive given in terms of sol. I; 1 g. sol. equiv. to 0.000446 g. As_2O_5. Determinations 11–22 inclusive given in terms of Sol. III; 1 g. sol. equiv. to 0.000494 g. As_2O_5.

Taken 0.0097 g. $FeSO_4.7H_2O$ equiv. to	0.0025 g. FeO
Taken	0.0116 g. As_2O_5
Found 0.0512 g. $Mg_2As_2O_7$ equiv. to	0.0113 g. As_2O_5
Error	0.0003
Taken 0.0193 g. $FeSO_4.7H_2O$ equiv. to	0.0050 g. FeO
Taken	0.0116 g. As_2O_5
Found 0.0153 g. $Mg_2As_2O_7$ equiv. to	0.0113 g. As_2O_5
Error	0.0003

Here we took as large a quantity of arsenic as we have found in any glass and much more oxide of iron than would be found in any but very special kinds of glass. It is evident that a quantity equal to 0.5 per cent FeO reckoned on a basis of 1 g. glass has no influence on the determination.

Effect of Ferric Iron on the Separation of Trivalent from Pentavalent Arsenic.—Further thinking on the real nature of the small differences which we call arsenic trioxide led to the suggestion that the true values of arsenic trioxide in the glasses might actually be greater than the values found, because a part of it may have been oxidized to arsenic acid by *ferric* iron in the process of solution of the glass. The following experiment was made to cover this point.

0.050 g. $Fe_2(SO_4)_3$ was put into the crucible with 5 cc. 1 : 1 H_2SO_4 and heated a half hour or more on the hot plate to make sure that any nitric acid, which the ferric sulphate sometimes contains, was removed. The crucible was then cooled and 0.0503 g. As_2O_3 was added. The crucible was covered and heated for an hour or more. Then it was cooled again, 5 cc. HF was added and the whole evaporated till white fumes appeared. The residue was tested rigorously with potassium iodide and hydrogen sulphide. No arsenic was found. Therefore all the arsenic was volatilized and none could have been oxidized by the ferric sulphate. Evidently then the presence of ferric iron does not interfere with the separation of the two forms of arsenic by hydrofluoric and sulphuric acids.

Effect of Chlorine in Glass on the Accuracy of the Separation of the Two Forms of Arsenic.—Most, if not all glasses, contain

chlorine, doubtless in the form of chloride. In the Jena glasses analyzed by us, the largest quantity of chlorine found was 0.06 per cent. In an American optical glass 0.16 per cent was found. Glasses made from material less carefully selected may contain still more. According to Dr. E. C. Sullivan, chief chemist of the Corning Glass Works, the largest quantity of chlorine which has been found in any glass in that laboratory is 0.14 per cent. Now since arsenic is volatilized *when either oxide* is heated with hydrochloric acid under favorable conditions, *e. g.*, during the evaporation in the silica determination in a glass, it is quite conceivable that arsenic acid should be reduced by hydrochloric acid and volatilized in the solution of a glass by sulphuric and hydrofluoric acids. (See footnote p. 742.) To test this point, weighed quantities of sodium chloride were heated with given amounts of arsenic acid, sulphuric and hydrofluoric acids. The crucibles contained:

Glass free from arsenic	1.00 g.
Arsenic acid solution, 10 cc., equiv. to	0.0058 g. As_2O_5
NaCl = 0.004 g. equiv. to	0.0025 g. Cl

This was evaporated to dryness in a covered platinum dish. 5 cc. HF was now added and when the salts had dissolved, 5 cc. 1 : 1 H_2SO_4 was also added and the whole evaporated to white fumes. The arsenic was then determined as usual.

11.64 g. iodine solution used in titration; 1 g. solution is equivalent to 0.000494 g. As_2O_5.

Taken	0.00580 g. As_2O_5
Found	0.00575 g. As_2O_5
Error	0.00005 g. As_2O_5

Again the following quantities of the same substances were used in the same way.

Glass free from arsenic	1.00 g.
As_2O_5	0.0029 g.
NaCl = 0.0080 g. equiv. to	0.005 g.
H_2SO_4 = 5 cc.	
HF = 5 cc.	

5.97 g. iodine solution used in titration.

Taken	0.00290 g. As_2O_5
Found	0.00295 g. As_2O_5
Error	0.00005 g. As_2O_5

These experiments show conclusively that quantities of chlorine of the magnitude found in glasses do not interfere with the separation of the two forms of arsenic.

Influence of Platinum Dissolved from the Crucible on the Separation of the Two Forms of Arsenic.—In the fusion required in the determination of total arsenic a small amount of platinum is dissolved which eventually is precipitated with the arsenic sulphide. This platinum sulphide is somewhat soluble in ammonia and ammonium carbonate. Since platinum is an element of two valencies it is conceivable that reduction by hydriodic acid and subsequent titration with iodine solution might consume a small amount of the latter. Two blanks were therefore made, in which 3 g. Na_2CO_3 and 0.1 g. KNO_3 were fused in a platinum crucible with 0.7 g. and 0.5 g. pure quartz, respectively. Each fusion cake was then treated exactly as in an arsenic determination. A minute black precipitate brought down by hydrogen sulphide was digested with ammonia and ammonium carbonate, oxidized by hydrogen dioxide, reduced and titrated.

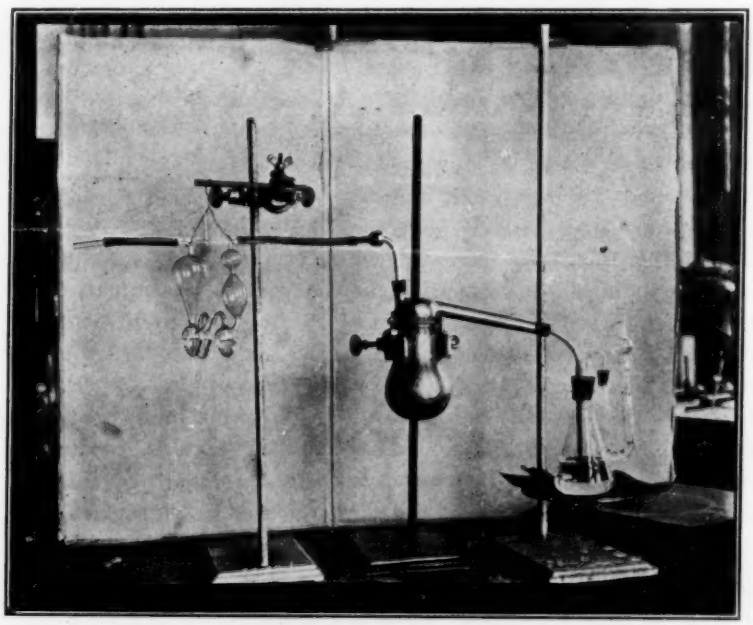
No. 1 required 0.16 g. iodine solution, equivalent to 0.08 mg. As_2O_5.
No. 2 required 0.10 g. iodine solution, equivalent to 0.05 mg. As_2O_5.

Still another blank was made by heating sulphuric acid and hydrofluoric acid in a platinum dish just as in the determination of pentavalent arsenic. The amount of iodine required in titration was 0.18 g., equivalent to 0.09 mg. As_2O_5. It is therefore obvious that the difference in the results obtained on any glass by the two methods cannot be accounted for by platinum derived from the crucible in fusion, nor can the difference be accounted for by any other influence which may be eliminated by making blanks, for the blanks are of the same order of magnitude.

Separation and Direct Determination of Trivalent Arsenic.—From a purely analytical point of view, it is perhaps a question of no great interest whether the small differences which we found between our series of determinations of total arsenic on the one

hand and pentavalent arsenic on the other really represented the quantity of arsenious oxide present; but in its relation to the chemistry of glass making, this question becomes a matter of more importance.

We were unable to find any considerable error in our results, but as we were still unconvinced of their meaning, we sought positive evidence in the matter by attempting to treat the glasses with hydrofluoric and sulphuric acids in such a way that the volatile material could be caught and examined. In principle, of course, the matter is perfectly simple, but the necessity of using hydrofluoric acid makes a glass apparatus unsuitable since the glass might contain arsenic and the quantity of arsenic in question is very small. Fortunately, we were able to get from the laboratory of the U. S. Geological Survey a small platinum still which could be satisfactorily adapted to the purpose. The head of the still, which is fitted to it by a taper joint, was made tight with



a rubber washer and brass clamps (Fig. 1). The distillate was caught in a caustic soda solution held in a receiver con-

nected to the still by an improvised gold tube and rubber stoppers. The volatile products are swept out of the still into the receiver by a current of air which enters the still through a small platinum tube. The joint between this tube and the head of the still was originally made with a perforated rubber stopper. This worked well when the still was very gently heated, but if the distillation was hurried the results were high, *i. e.*, some pentavalent arsenic was carried over into the receiver. The losses were partly mechanical undoubtedly, and in part due, as we suspected, to the reducing action of the rubber stopper which was at times badly attacked. The latter was, at any rate, eliminated by replacing the rubber stopper by a cork which was protected from the vapors of the still by a thin, close-fitting gold ferrule which made a sufficiently tight joint with the still. The mechanical losses were successfully avoided by dropping into the still, with the reagents and arsenical materials, a few pieces of crumpled platinum foil and 0.5–1.0 g. of lead sulphate. The still was heated by the aid of a radiator.[1]

For the most careful tests a gold bottle was substituted for the glass receiver which was always found to be attacked and which might have yielded a little arsenic to the solution.

With these safeguards the direct determination of arsenious arsenic in known mixtures with arsenic acid gave very accurate results. The determination is here a little more complicated than in previous cases because the arsenite solution now contains an excess of fluoride. If this solution were acidified and precipitated hot with hydrogen sulphide, the hydrofluoric acid would attack the glass container and might increase the quantity of arsenic. The alkaline solution was therefore evaporated to near dryness with a little hydrogen peroxide. This of course oxidized the arsenic and permitted the separation of excess hydrofluoric acid by fuming with sulphuric acid. (See p. 751.) The salt cake so obtained was cooled, dissolved in hot water and filtered, after which the arsenic was precipitated with hydrogen sulphide and determined as usual. The results of the separation of small quantities of arsenious acid from arsenic acid are given in Table 7.

[1] See Hillebrand, "Analysis of silicate and carbonate rocks," United States Geol Survey, *Bull.* **422**, 31.

TABLE 7.

Separation by distillation of As_2O_3 from known mixtures with As_2O_5 and determination of the former.

Grams iodine solution required.....	0.16	0.74	1.70	2.32	3.87	4.52
Equivalent to As_2O_3 in mg.....	0.07	0.3	0.7	1.0	1.6	1.9
As_2O_3 taken in mg.....	None	0.3	0.5	1.0	1.5	2.0
As_2O_5 taken in mg.....	116.0	116.0	58.0	11.6	58.0	58.0
Error.....	0.07	0.0	0.2	0.0	0.1	0.1

The necessity of refining the method to this point will be obvious if the reader bears in mind its purpose, which was to decide whether certain small differences between two methods for determining arsenic really and accurately represented arsenious oxide. The method was now applied to a chosen number of the glasses. The results, which are tabulated in Table 8, show

TABLE 8.

Direct determination of trivalent arsenic in glasses compared with the difference between pentavalent and total arsenic.

As_2O_3 in milligrams per gram of glass.

	Jena Optical.							Pittsburgh Spectacle Crown.
	1.	2.	7.	8.	9.	11.	13.	20.
Grams iodine solution required[1].....	1.47	0.84	1.37	0.60	0.91	1.28	0.28	2.47
Equivalent to mg. As_2O_3 (A).....	0.6	0.3	0.6	0.3	0.4	0.5	0.1	1.0
Difference between pentavalent and total arsenic mg. As_2O_3 (B)....	0.9	0.0	0.7	0.4	0.3	0.7	0.1	0.9
Difference between A and B in mg.....	0.3	0.3	0.1	0.1	0.1	0.2	0.0	0.1

not only that direct determinations of arsenious oxide in these glasses give positive results, but that these results are of the same order of magnitude as the differences in question. In five out of

[1] 1 g. iodine solution is equivalent to 0.000425 g. As_2O_3.

eight glasses tested the variation between the direct and indirect determination of arsenious oxide is only 0.1 mg. and in the other three the variation is only 0.3 mg. at the maximum.

It is obvious that the accuracy of the determination might be considerably increased by taking larger portions for analysis, but as our supply of material was limited and the method had been brought to a degree of precision quite sufficient for our purposes, the investigation was pursued no further.

II. Determination of Boric Acid.

The direct determination of boric acid in silicates has hitherto been a tedious process and for this reason this constituent is frequently not reported, or if known to be present is determined by difference. Such a procedure is of course very unsatisfactory since all the errors made in the determination of the other constituents fall upon the boric acid. In order to avoid this difficulty, we directed our efforts toward finding a satisfactory method for the direct determination of boric acid in the Jena optical glasses submitted to us for analysis.

Wherry's Method.—The method originated by Wherry[1] and modified by Sullivan and Taylor[2] seemed rapid and accurate and probably best adapted to our needs. We made repeated attempts to determine by the modified method the boric acid in a glass containing about 0.5 per cent B_2O_3, making double precipitations with $CaCO_3$. The results were erratic, and while we have not done enough work on the method to say that some modification of our procedure might not materially improve the results, the necessity of washing out the boric acid in an alkaline solution from bulky gelatinous precipitates is a fundamental objection to it. The tenacity with which such precipitates retain other substances is well known; then, too, we could not avoid the suspicion that with some combinations of elements a substance with the characteristics of boric acid might form insoluble compounds which could not be removed at all. We are aware that the method is used in the laboratories of some of the largest glass works and it is presumably valuable as a control

[1] Wherry and Chapin, *J. Am. Chem. Soc.*, **30**, 1687 (1908).

[2] Sullivan and Taylor, *J. Ind. Eng. Chem.*, **6**, 897 (1914).

method, but as a method of *high accuracy* it cannot be recommended for *general use*. Wherry himself has expressed the same opinion.

Electrometric Method.—Boric acid can be determined rapidly and accurately by the electrometric[1] method. In order to use this method, in the analysis of glasses, however, the boric acid must first be quantitatively separated from the other constituents in the glass, especially from the arsenic. If the arsenic is present as *arsenic* acid we have an acid whose strength[2] naturally vitiates the results, and, if present as *arsenious* acid, we have an acid which behaves much like boric acid in the presence of the mannite[3] which must be added to the solution when the electrometric method is used.

Chapin's Method.—After the fruitless efforts which we have recounted, Chapin's[4] method was considered. We may anticipate here by saying that for the determination of boric acid in silicates of such varying composition as the glasses, the method is, certainly at the present time, superior to all others. The description of the method may give one the impression that it is very tedious, but after the apparatus is once set up and the standard solutions are made, the determination can be carried out as rapidly as most of the analytical methods used in the analysis of silicates.

The method of Chapin is a combination distillation and titration method and consists in brief of the following procedure:[5] The powdered silicate is fused with Na_2CO_3 and the cooled melt taken up with 1 : 1 HCl. The boric acid thus set free is volatilized with pure methyl alcohol as methyl borate in the presence of granular anhydrous $CaCl_2$ which serves as a dehydrating agent. The distillates are treated with NaOH, either $N/2$ or $N/5$, de-

[1] J. H. Hildebrand, *J. Am. Chem. Soc.*, **35**, 861 (1913).

[2] Abegg's "Handbuch," Vol. III, part 3, p. 539, and Vol. III, part 1, p. 29.

[3] The large amount of alkali used up when As_2O_3 in the presence of mannite is treated with $Ba(OH)_2$, using phenolphthalein as indicator, proves this.

[4] *J. Am. Chem. Soc.*, **30**, 1691 (1908).

[5] The reader is referred to Chapin's description of the method for the necessary details, *J. Am. Chem. Soc.*, **30**, 1687 (1908).

pending on the amount of boric acid present. The NaOH combines with the boric acid and permits the removal of the methyl alcohol by distillation. The alkaline borate is treated with HCl and heated under the proper conditions to expel CO_2. The solution is now ready for the final titration, which is carried out as follows: The excess of HCl is neutralized with NaOH, using para-nitrophenol to indicate the end point. Mannite is now introduced and the titration of the boric acid carried out using a few drops of phenolphthalein as indicator.

Chapin tried out the method in the presence of such substances as fluorides, and the oxides of arsenic and zinc. These substances are often present as essential constituents of glasses. In every case his results show close agreement between the amount of boric acid taken and found. We have subjected this method to a rather thorough investigation and can in the main confirm his conclusions.

Determination of the Blank.—It was considered advisable to learn if boric acid could be satisfactorily determined under the usual laboratory conditions where one is forced to use glass flasks, such as Jena or Pyrex, which contain boric acid; and also if our chemicals contained boric acid. In the three experiments tabulated below all the flasks used were made of Jena glass. Three grams of Na_2CO_3 were treated with 12 cc. of 1 : 1 HCl in the decomposition flask and one gram of granular anhydrous $CaCl_2$ per cc. of liquid, added to the solution. The vapors of pure methyl alcohol were passed into the flask until about 200 cc. of the distillate had been obtained. For the final titration we used $Ba(OH)_2$[1] instead of NaOH, since the former can be prepared and maintained free from CO_2 much more readily than the latter. The $Ba(OH)_2$ was about $N/10$ and was standardized both against HCl and pure fused B_2O_3, using para-nitrophenol and phenolphthalein as indicators, the titration for the second end point being carried out as usual in the presence of mannite. On account of the volatility of B_2O_3 in a hot solution the titration must be carried out in the cold; therefore if it is necessary to add water to

[1] H. Will, *Arch. Pharm.*, **225**, 1101 (1887); E. Zschimmer, *Chem. Ztg.*, **25**, 442-67 (1901); Sullivan and Taylor, *J. Ind. Eng. Chem.*, **6**, 897 (1914).

the solution for rinsing purposes such water must be free from CO_2. Undue shaking of the solution must also be avoided on account of the sensitiveness of phenolphthalein to the CO_2 thus introduced. Under these conditions, both end points can be sharply determined. The results of the three experiments mentioned above are shown below:

Expt.	$Ba(OH)_2$ used. Cc.	Equiv. to B_2O_3. G.
1	0.20	0.0007
2	0.25	0.0009
3	0.20	0.0007

From these results it is evident that a blank must be made under the same conditions as those which prevail in an actual determination of boric acid. This blank may be due to several causes any one or all of which may be operative: (1) Boric acid may be present in the chemicals, or (2) it may be derived from the glass, (3) finally, the difficulty of getting sharp end points in the solution obtained after the distillation with methyl alcohol may also introduce a plus error. We have noticed repeatedly that the second end point in the final titration is never as sharp as in the titration in the pure aqueous solution used for the standardization of the $Ba(OH)_2$. This point will be brought up again later on.

The aqueous solution obtained after removing the methyl alcohol and acidifying were tested for B_2O_3 by the method of Bertrand and Agulhon.[1] We have found this method very satisfactory for small quantities. Boric acid was shown to be present in all our blanks.

Subsequently, we endeavored to determine the source of the B_2O_3. The glass decomposition flask was replaced by a platinum still, the glass condenser tube with one of silica glass, and the evaporation of the distillate carried out in a platinum vessel. All the other conditions were the same as those in the experiments just described. The titration with $Ba(OH)_2$,[2] which was

[1] Bertrand and Agulhon, *Compt. Rend.*, **157**, 1433 (1912).

[2] The $Ba(OH)_2$ used in these experiments was $^1/_5$ the strength of the $Ba(OH)_2$ mentioned in the experiments described above.

carried as usual in the presence of mannite, showed that under these new conditions our blank amounted to 0.7 mg., which is practically identical with results obtained above. We feel confident therefore that no appreciable amount of boric acid was derived from the glass parts of our apparatus.[1] It is probable, however, that this would not have been the case had fluoride been present.

It was also found that a small amount of $Ba(OH)_2$ was used up in passing from the first end point (para-nitrophenol) to the second (phenolphthalein), when the titration was carried out in distilled water free from CO_2. The amount of $Ba(OH)_2$ used was equivalent to 0.3 mg. It is evident therefore that the major portion of the blank is due to the boric acid contained in the chemicals. The amount of the blank obtained in the experiments was constant enough to encourage us to continue our work and determine the correction to be applied to our boric acid values.

In the following experiments known quantities of the boric acid used in the titration of the standard $Ba(OH)_2$, together with 3 grams of Na_2CO_3 and the other necessary reagents, were used. The boric acid was, as usual, volatilized with pure methyl alcohol.

TABLE 9.

Expt.	B_2O_3 taken. G.	$Ba(OH)_2$ used. Cc.	B_2O_3 found. G.	Excess. G.
1	0.0124	3.85	0.0134	0.0010
2	0.0434	12.70	0.0440	0.0006
3	0.0764	22.25	0.0772	0.0008
4	0.1085	31.56	0.1094	0.0009
5	0.1363	36.70	0.1274	0.0011

If the determination has been properly carried out the B_2O_3 found is always greater than that taken. The results also show that the excess is independent of the amount of boric acid taken. We therefore felt justified in applying this excess (average = 0.9 mg.) as a correction to the amount of boric acid found.

[1] Our experience on this point does not confirm Mellor's statement. See J. W. Mellor, "A Treatise on Quantitative Inorganic Analysis" (Griffin & Co., London), p. 586, footnote 2.

In two experiments we found that the amount of boric acid determined was less than the amount taken. This was shown to be due to the fact that the volume of the solution in the decomposition flask was larger than usual and therefore required more $CaCl_2$. It is well known that the ordinary anhydrous $CaCl_2$ has an alkaline reaction. The additional amount of $CaCl_2$ required in the experiments just mentioned rendered the solution alkaline and prevented the volatilization of part of the boric acid. In carrying out a determination it is well, therefore, to determine the amount of HCl required to neutralize the alkalinity of a unit weight of the $CaCl_2$ used and add sufficient HCl to the decomposition flask to insure an excess of acid.

This excess, however, should not be unduly large, else too great an amount of NaOH will be required for the neutralization of the acid in the distillate. It has been shown above that our blank was caused almost entirely by B_2O_3 in the reagents, hence the necessity of avoiding an undue excess of any reagent used in the method.

Influence of Impurities in Alcohol.—Chapin has called attention to the fact that commercial wood alcohol will not answer for the determination of boric acid. We have confirmed this and find that the difficulty is caused by a yellow-colored impurity in the distillates which renders an exact determination of the first end point in which para-nitrophenol is used, out of the question. Then, too, the second end point is so indistinct that one can never be sure when it has been reached. In this connection it was thought that possibly another pair of indicators might overcome this difficulty. We did not succeed in finding such a pair, but we did find that when pure methyl alcohol was used, methyl red and thymol blue[1] yielded results which were quite as good as those obtained with para-nitrophenol and phenolphthalein.

One of the more common impurities found in methyl alcohol is acetone. In order to find out if this substance was the cause of the difficulty the following experiments were carried out:

[1] Lubs and Clark, *J. Wash. Acad. Sci.*, **5**, 614 (1915).

Expt.	B_2O_3 taken. G.	Pure acetone in methyl alcohol.	B_2O_3 found. G.	Corrected. G.
1.....	0.0358	1 per cent	0.0364	0.0355
2.....	0.0528	5 per cent	0.0538	0.0529

In (2), the second end point was indistinct and somewhat difficult to determine, which was not the case in (1). The experiments show that while it is not advisable to use an alcohol which contains over 1 per cent of acetone, this impurity is not the cause of the difficulty.[1] Squibb's methyl alcohol (analytical reagent) and Mallinckrodt's pure methyl alcohol gave excellent results.

Influence of Arsenic as As_2O_3.—It is well known that glass usually contains arsenic. In the determination of boric acid in a glass relatively high in arsenic, part of the latter distills over with the methyl borate; it was therefore deemed advisable to investigate the effect of this arsenic on the boric acid determination. Varying amounts of pure As_2O_3,[2] together with boric acid, were introduced into the decomposition flask along with the necessary reagents. The arsenic carried over into the distillates was determined[3] after titrating the B_2O_3.

TABLE 10.

Expt.	B_2O_3 taken. G.	As_2O_3 taken. G.	B_2O_3 found (corrected). G.	As_2O_3 found. G.
1.....	0.0715	0.0110	0.0715	Trace
2.....	0.0702	0.0105	0.0701	0.0011
3.....	0.0743	0.0500	0.0767	0.0245
4.....	0.0795	0.1000	..	0.0568 (*a*)
				0.0110 (*b*)

In (1), the amount of HCl added was such as to neutralize all bases and leave an excess of about 0.5 cc. conc. HCl. The amount of boric acid found agrees well with that taken, thus showing that

[1] Mellor, *loc. cit.*, p. 586.

[2] See p. 746 for the method by which the As_2O_3 was prepared.

[3] See p. 745 for description of the methods used in making the analyses of arsenic.

the accuracy of the determination has not been influenced by the amount of As_2O_3 taken. In (2), the amount of HCl in excess was about 1 cc. of conc. HCl. The accuracy has not been appreciably affected, though the distillates contain an appreciable amount of As_2O_3. In (3), the amount of arsenic was increased and the excess of HCl was 2 cc. The end point in this case was very indistinct and the amount of boric acid found was greatly in excess of the amount taken. In (4), 3 cc. of conc. HCl were present in excess of the requirements. The boric acid could not be determined on account of the constant fading out of the second end point. The arsenic was determined separately in the first and second distillates. The amounts are shown in the table and are marked *a* and *b*.

It is evident from these results that if the amount of As_2O_3 present is small and the excess of HCl is only about 1 cc. the determination of boric acid is just as accurate as if no As_2O_3 had been present. The amount of As_2O_3 used in the first two experiments represents the maximum amount ordinarily found in *glasses*. If, however, the substance to be analyzed contains a large amount of As_2O_3 the determination of B_2O_3 becomes inaccurate or impossible unless the As_2O_3 is first oxidized to As_2O_5 in the manner suggested below. The behavior of As_2O_3 under these conditions is not surprising when we stop to consider the ease with which As_2O_3 is volatilized in the presence of HCl.

Influence of Arsenic as As_2O_5.—It also seemed worth while to know whether *pentavalent* arsenic interferes with the accuracy of the boric acid determination, especially as most of the arsenic in glass is in that form. The As_2O_5 used in these experiments was prepared in the manner described on p. 746.

Expt.	B_2O_3 taken. G.	As_2O_5 taken. G.	B_2O_3 found (corrected). G.	Arsenic as As_2O_3 in the distillate. G.
1	0.0762	0.0500	0.0765	0.0018
2	0.0745	0.0600	0.0746	0.0019

In both experiments 2 cc. of conc. HCl were present in excess. The results show that the presence of relatively large quantities

of As_2O_5 do not influence the accuracy of the boric acid determination. It is rather interesting to note that some arsenic was carried over into the distillate. This could not have been derived from As_2O_3 which might have been present in the As_2O_5, because the manner in which the As_2O_5 was prepared precluded the possibility of the presence of As_2O_3. It is well established that in the presence of concentrated HCl a partial reduction of the As_2O_5 to As_2O_3 takes place.[1] The presence of the trivalent arsenic is thus accounted for. On the basis of these results it appears advisable, where boric acid must be determined in a substance which contains a large quantity of trivalent arsenic, to oxidize the latter in a solution made distinctly alkaline with NaOH before distilling off the boric acid.

Since certain types of glasses contain fluorine, an experiment was carried out in order to learn if this element introduced any disturbing features. A solution containing NaF and B_2O_3 was made alkaline with 20 cc. of $N/2$ NaOH, evaporated to dryness, acidified with HCl and distilled as usual.

B_2O_3 taken.	NaF.	$Ba(OH)_2$ used. Cc.	B_2O_3 found (corrected).
0.1500	0.200	40.70	0.1517

The determination of the second end point was not as sharp as usual, and the difference between the amount found and taken is greater than the experimental error. Chapin carried out a similar experiment, using, however, a smaller amount of NaF, and obtained very close agreement between the amount of B_2O_3 taken and found. This indicates that the method is very accurate when relatively small amounts of fluorides are present. The method is, however, useful even under the adverse conditions of our experiment.

When small quantities of B_2O_3, say 2 mg. or less, are to be determined, it will be best to use the method described by Bertrand and Agulhon,[2] provided all the chemicals are known to be

[1] Abegg's "Handbuch," Vol. III, part 3, p. 539.

[2] Bertrand and Agulhon, *Compt. Rend.*, **157**, 1433 (1913).

free from B_2O_3.[1] The method is a very sensitive one and must be carried out with great care.

Finally, we will present a few results showing the close agreement between the determinations when carried out by this method and when the proper correction is applied, on different samples of the same glass. In the table below are tabulated a series of three experiments each on a glass relatively high in B_2O_3 and on one low in B_2O_3.

TABLE II.

Glass.	Amount of sample. G.	$Ba(OH)_2$ used. Cc.	B_2O_3 found. G.	Corrected. G.	% of B_2O_3.
1.....	0.5000	34.95	0.1311	0.1301	26.02
	0.3000	21.10	0.0792	0.0782	26.06
	0.5000	35.00	0.1313	0.1313	26.06
2.....	1.0000	2.10	0.0073	0.0064	0.64
	1.0000	2.20	0.0076	0.0067	0.67
	1.0000	2.25	0.0078	0.0069	0.69

In the course of our work we have carried out about 50 determinations of boric acid by the Chapin method and have been greatly impressed by its neatness and accuracy.

III. Determination of Some Other Constituents.

A considerable number of the constituents of glass may be satisfactorily determined in exactly the same way as is done in rocks. This is true of silica, chlorine and manganese, also of calcium, magnesium and the alkalies, except when boric acid is present.[2] In the presence of boric acid only one modification of the usual procedure is necessary. (See p. 779.) But glass contains other elements in addition to those considered in the foregoing pages, the separation and determination of which are rarely called for in rock analysis; or elements which, on account of their quantity or their association with other elements, present

[1] No doubt for very small quantities of B_2O_3, it will be well to avoid the use of glass apparatus or at least the use of such kinds of glass apparatus as contain B_2O_3.

[2] Some glasses contain phosphoric acid; these, of course, demand special methods. We have had no experience with them.

special difficulties to the analyst. We shall make no attempt to cover the whole field—only such portions of it as have come within our own experience, where we have found difficulties and have gained some knowledge of the accuracy of certain methods.

1. Determination of Iron in Optical Glasses.—Since a very little iron colors glass appreciably and lowers its transmission, only a very small amount is permissible in an *optical* glass. The accurate determination of this iron demands several precautions; care must be taken to exclude iron from all outside sources and to avoid loss of iron by occlusion in those precipitations which necessity demand before iron can be determined. First a special sample of about 5 g. of the glass should be prepared by crushing in *agate* instead of steel; a crucible of the purest platinum should be used in the various operations requiring one, especially when the fusions are made. Finally a suitable blank must be made.

Two or three grams of the sample are decomposed with about 3 cc. 1 : 1 sulphuric acid and 5 cc. hydrofluoric acid just as in the determination of pentavalent arsenic. Cool, transfer the residue to a beaker with water and boil till any insoluble sulphate becomes filterable. Filter into a 150 cc. flask, wash, and save the precipitate which may contain as much as 50 per cent of the total iron. Precipitate the filtrate hot with hydrogen sulphide. Thus arsenic and the remaining lead[1] are removed. If zinc is present, proceed according to Waring,[2] *viz.*, add to the solution before precipitation with hydrogen sulphide a drop or two of methyl orange, neutralize with sodium carbonate and add 0.3 to 0.5 cc. excess of 50 per cent formic acid. In a solution of this acidity zinc sulphide is precipitated in a denser form than in an alkaline solution. Waring draws up the conducting tube above the level of the liquid and corks the flask tight, thus leaving the liquid under a slight pressure of the gas over night. The filtrate from the zinc sulphide which ordinarily contains the major part of the iron is boiled to expel hydrogen sulphide and precipitated by boiling with pure ammonia and a few cc. of hydrogen peroxide.

[1] The amount of lead not precipitated by sulphuric acid is appreciable when the sulphate is filtered immediately after precipitation.

[2] *J. Am. Chem. Soc.*, **26**, 4 (1904).

If the glass contains lead the insoluble sulphates should first be leached on the filter with a hot concentrated *ammoniacal* solution of ammonium acetate which should previously be filtered if it contains any iron whatever. When the lead sulphate has all been washed through by this means, the residue, whether it contains barium sulphate or not, should be incinerated in the platinum crucible and then fused for a short time with a *weighed portion* of pure potassium or sodium bisulphate. From the cooled mass the iron is extracted by hot dilute sulphuric acid and precipitated like the major portion. Both the very small precipitates of ferric hydroxide are then filtered and washed on the same filter, incinerated in the pure platinum crucible and fused with a *weighed portion* of pure potassium bisulphate for a few minutes at a comparatively low temperature (under a red heat). All the iron is easily dissolved. The remainder of the determination is done according to Hillebrand,[1] *i. e.*, the fused cake is dissolved in water (no sulphuric acid is needed here) and the solution reduced by hydrogen sulphide; the small precipitate of platinum sulphide filtered off, and the hydrogen sulphide expelled from the filtrate by boiling in a current of carbon dioxide which is *washed by a solution of copper sulphate*. This operation is very conveniently carried out in a glass-stoppered wash bottle.

The cold solution is titrated by a very dilute solution of potassium permanganate with the aid of a weight burette. The permanganate is best standardized by sodium oxalate. The blank should be carried out as nearly as may be like the determination itself; especially should the same quantities of hydrofluoric acid and potassium bisulphate be used and the fusions should be conducted in a similar manner as to time and temperature.

Some results are given in Table 12 which may be of interest in showing the minute quantities of iron in optical glasses and the remarkable uniformity of the Jena glasses.

2. The Determination of Zinc.—Zinc may of course be determined in the filtrate from silica, or preferably in the same sample as arsenic and lead.[2] One or two grams of the glass are

[1] United States Geol. Survey, *Bull.* **422**, 107.

[2] When barium is present the procedure on p. 777 may be followed.

TABLE 12.

Determination of Iron in Some Optical Glasses.

	Jena Optical Glasses.								American Optical Glasses.			
	1.	2.	3.	4.	5.	6.	9.	10.	1.	2.	3.	4.
Weight of glass taken	2 g.	2 g.	2 g.	2 g.	3 g.	3 g.	3 g.	3 g.	3 g.	2 g.	2 g.	3 g.
Grams $KMnO_4$ solution[1] required	0.41	0.56	0.60	0.39	0.90	0.62	0.92	0.87	1.49	1.18	0.88	1.27
Grams $KMnO_4$ solution in blank	0.16	0.16	0.16	0.16	0.13	0.16	0.13	0.13	0.16	0.16	0.17	0.13
Grams $KMnO_4$ equivalent to iron	0.25	0.40	0.44	0.23	0.77	0.46	0.79	0.74	1.33	1.02	0.71	1.14
Grams $KMnO_4$ solution per g. glass.	0.12	0.20	0.22	0.12	0.26	0.15	0.26	0.25	0.44	0.51	0.35	0.38
Per cent of iron cal. as Fe_2O_3[2]	0.011	0.018	0.020	0.011	0.020	0.013	0.020	0.019	0.040	0.046	0.032	0.029

[1] $KMnO_4$ Sol. I used for Jena glasses 1, 2, 3, 4 and 6; American glasses 1, 2 and 3; 1 g. sol. equivalent to 0.00091 g. Fe_2O_3. $KMnO_4$ Sol. II used for Jena glasses 5, 9 and 10; American glass 4; 1 g. sol. equivalent to 0.00078 g. Fe_2O_3.

[2] The results are believed to be accurate within 0.005 per cent.

weighed out, decomposed by hydrofluoric and sulphuric acid and the product evaporated to white fumes. The residue is cooled, transferred to a beaker and diluted. If all is soluble the solution is used directly for the zinc determination. If barium is present the solution should first be boiled for some time to render the sulphate filterable, while if either barium or lead is present the solution should be set aside for the night to insure complete precipitation. The precipitate is then filtered on a Gooch crucible if lead is present, otherwise on paper; the washing in either case following the well known methods. The filtrate and washings[1] are taken for the determination of zinc.

In this solution the arsenic may be precipitated first by hydrogen sulphide or both arsenic and zinc may be precipitated together by the same reagent. In either case before zinc is precipitated, the acidity of the solution should be reduced according to Waring,[2] and the zinc sulphide brought down in a hot and slightly acid solution. If the sulphides of zinc and arsenic are precipitated together, the precipitate is washed with hot water, the funnel covered with a watch glass and the zinc sulphide dissolved by pouring cautiously under the cover a little hot 1 : 1 hydrochloric acid, while the filtrate is caught in a beaker. After the filter has been thoroughly washed with hot water, it is well to dissolve the arsenic sulphide by pouring a few cc. colorless ammonium sulphide directly on the filter and washing into a separate beaker. A very little zinc sulphide may be left and it is safe, therefore, to treat the filter again with a little hot, dilute, hydrochloric acid, adding the filtrate to the zinc solution. After the hydrogen sulphide has been boiled out of the latter the zinc may be satisfactorily determined by several methods.

Sullivan and Taylor[3] add a little more than the required quantity of sulphuric acid, evaporate to dryness, heat to redness and weigh the sulphate. Their results were very good. In some of our determinations we have made a double precipitation of the zinc by sodium carbonate in very slightly alkaline solution, according

[1] Excepting of course the final washing with alcohol when lead is present.

[2] *Loc. cit.*

[3] *J. Ind. Eng. Chem.*, 1, 476, (1909).

to Treadwell,[1] filtering on a Gooch filter and heating inside a large porcelain crucible[2] to the highest temperature of the Bunsen burner.[3]

0.1000 g. pure metallic zinc by this method gave 0.1245 g. ZnO equivalent to 0.1007 g. zinc. The following duplicate results on glasses were obtained by separating the zinc in the manner described, precipitating the redissolved sulphide as carbonate and weighing as oxide:

	ZnO found.
Jena optical glass No. 3.....	1.00 per cent 0.96 per cent
Jena optical glass No. 6.....	8.46 per cent 8.61 per cent
Jena optical glass No. 8.....	1.14 per cent 1.24 per cent
Jena optical glass No. 15.....	1.42 per cent 1.46 per cent

A little more accurate but not quite so rapid as the carbonate method is the electrolytic method. If the latter is to be employed, the chloride solution obtained by dissolving the zinc sulphide is first fumed with sulphuric acid in slight excess, cooled and diluted to 100 cc. Pure caustic soda is now added till the precipitated zinc hydroxide is redissolved; then acetic acid in quantity sufficient to precipitate and again dissolve the hydroxide. The solution is acidulated with 0.5 cc. glacial acetic acid, diluted to 150 cc. and electrolyzed at room temperature. To secure good results the following points must be heeded: In the first place zinc cannot be precipitated directly on platinum without alloying with the platinum somewhat and roughening its surface. Also the cathode must be smooth if a uniform, firmly adhering deposit is to be obtained.[4] To obviate these difficulties the platinum cathode is carefully coated with copper. This may be done by electrolyzing

[1] Treadwell, trans. by Hall, II, 4th ed., Wiley & Sons, N. Y., p. 142.

[2] *Ibid.*, p. 27.

[3] An electric oven of suitable type was not at that time available.

[4] H. J. S. Sand, *J. Chem. Soc. London, Trans.*, **91**, 383 (1907).

a copper sulphate solution containing 2 per cent nitric acid at a suitable current density. We used a rotating gauze cathode of about 85 cm^2. available surface, gradually increasing the current from 0.25 to 1.00 amp. over a period of 20 minutes. The cathode was washed with water, then successively by alcohol and ether and dried in a current of air at room temperature. Finally, in the electrolytic precipitation of zinc, a current under 4 volts must be used; otherwise hydrogen will be liberated, the metal will be spongy and will not cling to the electrode. Heeding the above precautions, using the rotating[1] gauze cathode described and electrolyzing with a current which was gradually raised from 0.25 to 2.5 amp. at a maximum of 4 volts, thirty minutes proved sufficient for the deposition of over 0.300 g. of zinc, which adhered well to the cathode. It is unwise to precipitate much more than this amount on a cathode of this area (85 cm^2.), since larger deposits show a tendency to flake off. The zinc is washed without breaking the current and dried exactly like the copper deposit mentioned above.

A standard sample of zinc from the U. S. Bureau of Standards gave the following results:

	Zinc taken. G.	Found. G.
1	0.3227	0.3230
2	0.3227	0.3232
3	0.2154	0.2159
4	0.2154	0.2154

In the first three experiments the zinc was simply dissolved in such an amount of sulphuric acid as to leave about 1 cc. pure H_2SO_4 in excess, after which the procedure was exactly as prescribed above. In the fourth experiment the zinc was precipitated as sulphide, dissolved and further treated like the other three. A comparison of the carbonate and electrolytic methods on an American optical glass follows:

[1] See Gooch and Medway, *Am. J. Sci.*, [4] **15**, 320 (1903); *Ibid.*, **18**, 56 (1904); Exner, *J. Am. Chem. Soc.*, **25**, 896 (1903).

	Carbonate method.	Electrolytic method.
ZnO found.....	1.17 per cent 1.12 per cent	1.19 per cent 1.20 per cent 1.25 per cent

Though we have not tried it, the electrometric method for zinc of Bichowsky[1] appears rapid and accurate and would have decided advantages where many determinations were to be made.

3. Determination of Lead and Barium Occurring Together.—In a glass which contains both lead and barium we have found it best to determine the two together as sulphates; then in a separate portion to determine the barium directly and thus obtain the lead by difference. The lead may also be determined directly but this is more difficult. The details follow:

A weighed portion of glass is decomposed by sulphuric and hydrofluoric acids and evaporated till all the hydrofluoric acid is driven out. The pasty mass after cooling is transferred to a beaker by a jet of water, diluted to about 150 cc., boiled and left to stand over night. The filtering, washing and heating of the precipitate are carried out exactly as with pure lead sulphate.

Barium and lead sulphates cannot be separated by ammonium acetate solution; some of the former is sure to dissolve with the lead sulphate. Barium is therefore determined in a separate portion of glass which is fused with sodium carbonate. The silica is separated as usual, arsenic and lead are precipitated as sulphides by Waring's method,[2] the alumina, iron, etc., are precipitated by ammonium sulphide, and in the final filtrate from which the hydrogen sulphide has been boiled out the barium is determined as usual. In accurate work it should be noted that the barium sulphate, obtained either by precipitation from dilute solution, or by decomposition of the glass with sulphuric and hydrofluoric acids, always occludes some soluble sulphate and the weight is therefore too high. In two barium glasses which contained less than half a per cent of Na_2O, the barium sulphate

[1] *J. Ind. Eng. Chem.*, **9**, 668 (1917).

[2] *Loc. cit.*

obtained in the latter way contained the following impurities:[1]

0.6293 g. $BaSO_4$ glass No. 7 contained 0.0052 g. Na_2SO_4.
0.7140 g. $BaSO_4$ glass No. 8 contained 0.0061 g. Na_2SO_4.

The errors in the percentage of BaO in the above determinations would amount to 0.17 and 0.20 per cent, respectively.

In case a direct determination of lead is desired, the glass should be fused with sodium and potassium carbonates *at the lowest possible temperature* to avoid volatilization of lead oxide. The loss is then very small, if appreciable. The silica is now removed in the usual way except that the operator should wash it more carefully with hot water to remove the lead chloride. In any event it is wise to look for lead in the silica when the latter is volatilized with sulphuric and hydrofluoric acids. The residue should be carefully fused with a very little soda and added to the lead chloride solution. The latter is now made sufficiently acid and precipitated hot with hydrogen sulphide. After standing, the lead sulphide is filtered on a *small* filter, washed thoroughly, and transferred by a jet of water to a small casserole in which it is dissolved in nitric acid and finally evaporated to white fumes with sulphuric acid. The further treatment of the precipitate is carried out as usual, and the little lead sulphide which clings to the filter on which it was washed must be burned at a low temperature in a small tared porcelain capsule and finally fumed with a drop or two of sulphuric acid. The weight of the lead sulphate thus obtained is added to that of the main portion. Sullivan and Taylor[2] obtain results on lead 0.2 to 0.3 per cent lower when it is determined in the filtrate from silica than when it is determined by decomposing the glass with oxalic and hydrofluoric acids. Our results are similar when sulphuric is substituted for oxalic acid. Thus a glass which gave by the latter method $\left.\begin{matrix}35.26 \text{ per cent} \\ 35.26 \text{ per cent}\end{matrix}\right\}$ PbO, when fused with soda and heated further as described above, gave 35.13 per cent PbO.

A second glass, which by the first method gave 41.64 per cent PbO, gave 41.31 per cent by the second. The lower results

[1] For the method used in this determination see Allen and Johnston, *J. Am. Chem. Soc.*, **32**, 588 (1910).

[2] *Loc. cit.*

obtained by the second method are not necessarily due to the volatilization of lead in the fusion; they are quite as likely due to mechanical losses in the more complicated procedure which this method demands.

4. Separation of Alumina from Barium and Calcium.—Optical glasses not infrequently contain alumina in amounts ranging from 0.5 per cent to 5.0 per cent and sometimes much more. The precipitated alumina accompanied as it is by almost no iron is very difficult to filter,[1] yet when an alkaline earth is present it should be twice precipitated. One of us prefers to precipitate the first time cold with ammonium sulphide, by making the filtrate from zinc and arsenic, which already contains hydrogen sulphide, barely ammoniacal and allowing it to stand over night while the other makes a double precipitation with ammonia. However precipitated, *every filtrate* from the alumina should be evaporated to a small volume on the water bath to make sure no alumina is lost. If any appears it is filtered on a separate filter.

It is possibly not so generally known as it should be that ammonium hydroxide which has stood in glass for any considerable time invariably gives too high results when used to precipitate iron and alumina. Its freedom from silica and alumina or any other impurity which might interfere with the determination should be insured, after which the ammonia should be kept in ceresine or gold bottles.

5. Analysis of Glasses Containing Boric Acid.—Chapters on the analysis of glass including borosilicates, though not found in ordinary text-books on analysis, are given by Classen[3] and by

[1] Since iron is determined in a separate sample it would doubtless be better to add to the solution, before the alumina is precipitated, a small, measured volume of a dilute standard ferric chloride solution since, as is well known, an alumina precipitate containing several per cent of iron gives no trouble of this kind.

[2] The ammonia water used in this laboratory is made as follows. Liquefied ammonia gas is purchased in large steel cylinders from which small distributing cylinders of similar kind are filled. The gas is washed in a little water and absorbed in distilled water contained in a gold bottle packed in ice.

[3] "Ausgewählte Methoden der Analytischen Chemie," *Braunschweig*, 1901, I, 609.

Lunge.[1] The determination of boric acid itself we have already dealt with (p. 761). For the removal of boric acid where it would interfere with the determination of other elements, the same principle is utilized, *i. e.*, volatilization of the boric acid by methyl alcohol partially saturated with hydrochloric acid gas.[2] To guard against the precipitation of boric acid along with alumina, lime or magnesia, the boric acid should be removed in the progress of the silica determination. When the solution has been evaporated to dryness the *second time* to remove the last of the silica, cool the dish and add 25 cc. or so of the methyl alcohol solution, cover the dish and evaporate again on the steam bath. Repeat the operation, finally rinsing off the cover into the dish. Lunge recommends evaporating 3 or 4 times with methyl alcohol, but so far as our experience goes, two evaporations are sufficient.

Classen and Lunge both determine the alkalies in glass by Berzelius' method, in which the boric acid is volatilized as fluoride along with silica. More satisfactory is the method of J. Lawrence Smith.[3] In the decomposition of the glass by this method the boric acid is retained, and must be removed in a subsequent operation. When in the course of this method the chlorides of ammonium and the alkalis have been evaporated to dryness on the steam bath, 10 cc. of the methyl alcohol solution should be added and evaporated with the dish covered. One repetition is all that is necessary, in most cases, for the complete removal of the boric acid. In case of doubt it is a simple matter to repeat the operation on the *weighed* chlorides.

6. Determination of Moisture.—In the complete analysis of a glass it must be remembered that fine mineral powders generally absorb moisture from the atmosphere, the quantity absorbed by any particular mineral depending upon the fineness of the powder, *i. e.*, upon the extent of its surface. It may be surmised that glasses on account of their alkali content would be specially liable to absorb water. On this account the glass should be

[1] "Chemisch-technische Untersuchungsmethoden," *Berlin*, **1904**, I, 666.

[2] Jannasch and Heidenreich, *Z. anorg. Chem.*, **12**, 208.

[3] *Am. J. Sci.*, [3] **1**, 269 (1871). The method is described also by Hillebrand, *loc. cit.*, p. 171; H. S. Washington, "The Analysis of Silicate Rocks," 3d Ed., Wiley & Sons, N. Y., p. 193 and by Treadwell-Hall, p. 496.

crushed for a moment only, either in a hardened steel or an agate mortar, and then screened, the operation being repeated till sufficient powder is obtained. In this way very fine powder is almost entirely eliminated and only a minimum of moisture is absorbed. Optical glass powders prepared in this way gave the following losses when heated for a few minutes in a covered crucible over a Bunsen burner:

MOISTURE IN GLASS SAMPLES.

	Jena Glasses.										American Glasses.			
No. of glass	1	2	3	4	5	6	12	13	14	15	1	2	3	4
Per cent loss	0.06	0.09	0.20	0.08	0.03	0.14	0.15	0.08	0.08	0.16	0.06	0.10	0.06	..

Two other glass samples, which were inadvertently left in a mechanical grinder for several hours and were consequently very fine, lost on heating 0.68 per cent and 0.88 per cent, respectively.

The following experiments made for another purpose prove that the loss is unquestionably water. A certain glass, which lost 0.10 per cent when heated over a burner, was fused in a Gooch tubulated platinum crucible[1] with dry sodium carbonate, the moisture expelled by dry air and *absorbed by calcium chloride.*

From 1 g. glass was thus obtained 0.9 mg. H_2O = 0.09 per cent.
From 2 g. glass was thus obtained 2.2 mg. H_2O = 0.11 per cent.

7. Gases in Glass.—Low results in the analytical summation of certain glasses led us to consider the question whether gases occur in glass in appreciable quantity. Judging from its composition and the materials used in the manufacture of glass we supposed carbon dioxide was most likely to be found. We selected for the test a glass which from its high content in lime and alkali we believed would have a stronger tendency to retain this gas. 14.73 per cent CaO, 10.37 per cent Na_2O and 0.44 per cent K_2O were found by analysis. For the determination of carbon dioxide we used Borgström's modification[2] of the ordinary method, in which he decomposes the silicate by a dilute solution of hydro-

[1] *Am. Chem. Jour.*, **2**, 247 (1880); Hillebrand, *Bull.*, **422**, p. 78.
[2] *Z. anal. Chem.*, **53**, 685 (1914).

chloric and hydrofluoric acids. The gaseous mixture expelled from the decomposition vessel was driven through the usual train of absorbents. Borgström made three blanks in which his soda-lime tube gained from 0.8 to 1.6 mg. This amount he finds is no less when hydrochloric acid alone is used in the decomposition of the mineral.

Since the material which we had to test was *glass*, glass was excluded from certain parts of our apparatus. We used a platinum decomposition vessel and a water-jacketed lead tube as a condenser. Using Borgström's acid mixture in a blank experiment with this apparatus we found a gain of 1.4 mg. in the soda-lime tube. When 3 g. glass was heated in the same way for the same time the gain was 1.7 mg., showing that the carbon dioxide in this glass was small if appreciable. More than that, it is impossible to say on account of the large blank which the method involves.

Far more satisfactory is the following experiment carried out by our colleague Mr. E. S. Shepherd who has had unusual experience in work of this character. Mr. Shepherd very kindly tested the glass in question for gases. A large sample of the glass powder was weighed into a platinum boat which was heated in an evacuated silica glass tube at 1200°. The gases were pumped out and analyzed. Before the gases were measured they were drawn through an absorption tube containing silver oxide[1] and potassium carbonate. 0.0025 g. SO_2 equivalent to 0.87 cc. under standard conditions was removed. This is not included in the analysis.

6.577 g. glass gave 6.55 cc. gas measured under standard conditions. The analysis gave the following volume percentages:

O_2 =	64.2 per cent
CO_2 =	24.2 per cent
CO =	3.5 per cent
H_2 =	3.9 per cent
N_2 =	4.1 per cent
	99.9

A small fraction of the CO_2, less than 1 cc. at the most, may come from the potassium carbonate through decomposition by

[1] According to Mr. Shepherd, this method of separating SO_2 originated by him is not perfectly sharp but better than any other.

SO_2. Uncorrected the total carbon dioxide amounts to 0.05 weight per cent of the glass, while the total gas amounts to 0.15 weight per cent. If the reader cares to speculate on the source of the different gases it may be stated that the glass contained 0.74 per cent SO_3 which might give rise to the sulphur dioxide and a very little of the oxygen. It contained no arsenic. Whether nitrate was used in the manufacture we do not know. It was not an optical glass. The obvious fact is that glasses may contain an appreciable amount of gas most of which would probably not be included in an ordinary analysis *in any form*.

Composition of the Jena Optical Glasses.—This paper is chiefly concerned with analytical methods, but it will not be out of place to recall the purpose for which the work was originally undertaken, namely, to get information which might be of value in establishing the optical glass industry in this country. The Jena glasses were selected for investigation because of their world-famed excellence; because they are especially well known to scientists through the valuable publications of O. Schott and others; and because a large number of them were immediately available to us.

Table 13 contains nine analyses of Jena optical glasses. Nearly as many more were actually made but those given are typical. About half of them are virtually complete, so far as we know, except for the determination of gases which they probably contain. The summations of the remainder would be raised several tenths of a per cent by the addition of magnesia, sulphur trioxide, chlorine and moisture.

One American optical glass, 3*a*, is included in the table. It is evidently a copy of No. 5 and is practically as good as its prototype. This glass is also of interest because it contains no arsenic. The most obvious information to be gained from the analyses of the Jena glasses is that they must have been made from very pure raw materials, for the impurities lime, magnesia, sulphur trioxide, chlorine and iron are all present in insignificant quantities. There is practically no iron and extremely little chlorine and sulphur trioxide which in certain glasses are liable to cause milkiness. It is also a safe inference that the pots used must have been not only very low in iron but very refractory,

TABLE 13.
Analyses of Optical Glasses.

Our number	1	3	4	5	3a	8	9	10	11	13[1]
Schott's number	O3832	O154	O144	O167	——	O2071	O1209	O227	O722	O578
Optical constants n_D	1.5164	1.5711	1.5100	1.6163	1.6162	1.6091	1.6095	1.5409	1.5795	1.5832
Optical constants ν	64.0	43.0	64.0	36.6	36.6	58.8	56.8	59.6	53.8	46.3
SiO_2	69.58	54.75	72.15	46.12	46.32	34.56	40.17	59.13	45.02	49.80
B_2O_3	9.91	0.45	5.88	....	...	10.96	5.96	3.04	4.50	....
As_2O_5	0.22	0.14	0.20	0.25	None	0.55	0.49	0.34	0.55	0.51
As_2O_3	0.09	0.06	0.08	0.04	None	0.04	0.03		0.06	0.01
SO_3	0.08	...	0.12	0.10	...	...	....	...	....	....
Cl	0.06	0.06	0.06	....	...	...	....	...	...	....
Na_2O	8.44	4.31	5.16	1.72	2.48	0.21	0.13	3.16	0.64	1.24
K_2O	8.37	7.99	13.85	6.78	5.63	0.09	0.03	9.70	6.80	8.20
MgO	0.07	None	0.07	....	Trace	...	....	...	....	....
CaO	0.07	0.05	2.04	0.07	0.25	...	0.03	0.13	....	....
BaO	2.54	1.64	None	....	None	46.91	42.35	19.25	22.39	13.36
MnO	None	None	None	None	0.004	...	None	None	None	None
ZnO	None	0.96	None	....	None	1.14	8.17	5.00	15.53	8.03
PbO	None	29.30	Trace	45.13	45.03	None	None	None	4.70	18.74
Al_2O_3	0.04	0.04	0.04	0.06	0.02	5.02	2.79	0.11	0.09	0.05
Fe_2O_3	0.01	0.02	0.01	0.02	0.03		0.02	0.02		0.01
H_2O	0.06	0.20	0.08	0.03	0.06	...	....	...	....	0.08
	99.54	99.97	99.74	100.32	99.82	99.48	100.17	99.88	100.28	100.03

[1] For analysis No. 13, the authors are indebted to Dr. E. Posnjak.

for the glasses are almost free from alumina except where it has obviously been added to the batch.

The authors wish to express their thanks for the loan of a number of platinum utensils by the chemical laboratory of the U. S. Geological Survey, which materially facilitated the work.

SUMMARY.

Arsenic.

1. An accurate method for the separation and determination of both trivalent and pentavalent arsenic in glasses is described. (1) The separation depends on the volatilization of the trivalent arsenic as AsF_3 when the glass is heated with hydrofluoric and sulphuric acids, while the pentavalent arsenic remains in the residue. (2) The latter is determined by precipitation as sulphide which is then oxidized to arsenic acid, reduced by hydriodic acid and titrated with a standard iodine solution. (3) The trivalent arsenic is determined by difference between the pentavalent and total arsenic. The determination was controlled by direct determination with the aid of a platinum still. (4) The total arsenic is determined by fusing the glass with sodium and niter, removing the silica and excess nitric acid by evaporation with sulphuric acid and subsequent filtration; and finally proceeding as outlined in (2).

2. These methods for arsenic in glasses are generally applicable to substances in which the arsenic can be transformed into sulphide without loss, and are highly accurate.

3. A comparison of the iodometric method and the magnesium pyroarsenate method for arsenic in glasses is made. The former has the advantage in accuracy, and also in speed except where occasional determinations are called for.

Boric Acid.

1. For the determination of boric acid we have found that Chapin's method is very reliable and yields highly accurate results.

2. It has been shown that in order to obtain very accurate results, a "blank" must be made and the value applied as a correction to the amount of boric acid found. The correction is small and for ordinary work can be neglected.

3. The accuracy of the method is very appreciably affected by relatively large amounts of *arsenious* acid but not by *arsenic* acid. Boric acid can therefore be satisfactorily determined in the presence of large amounts of arsenious acid by oxidizing the solution with H_2O_2 after making it distinctly alkaline with NaOH.

4. Relatively large amounts of fluorides appreciably affect the accuracy of the determination but do not seriously impair its usefulness for ordinary work.

Other Determinations.—Our experience with the following cases in glass analysis is detailed: (1) the determination of the minute quantities of iron in *optical* glass; (2) the separation and determination of zinc; (3) the separation and determination of lead and barium occurring together; (4) the separation of calcium or barium from relatively large quantities of aluminum occurring with almost no iron; (5) the determination of those elements in boric acid glasses with which the boric acid interferes.

Attention is called to the universal presence of hygroscopic moisture in powdered glass samples.

Some data by Mr. E. S. Shepherd on gases in glass are given.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C., January 15, 1919.

THE CONDITION OF ARSENIC IN GLASS AND ITS ROLE IN GLASS-MAKING.

By E. T. Allen and E. G. Zies.

The condition of arsenic in glass has been a mooted question with glass-makers. O. Schott[1] of the Jena glass works regarded all the arsenic in *optical* glass as present in the form of arsenate which, he believes, is a product of the reaction between the arsenious oxide and the alkali nitrate of the batch. Where nitrate is not added to the batch it is Schott's opinion that the arsenic is entirely volatilized from the molten glass; in other words that glass never contains arsenic in the form of the lower oxide. On the other hand, W. Rosenhain[1] of the Chance Glass Works reasoned from the general chemical behavior of arsenic that glass must contain only the trivalent form.

F. Gelstharp[2] found experimentally that when arsenious oxide was fused with sodium carbonate in an open crucible at 940°, a part of it was volatilized, and, of the remainder, the major part was oxidized to arsenate. When arsenious oxide was heated with calcium carbonate to 1090°, again a portion of the arsenic was lost, while the rest was all oxidized to arsenate. Thus it appears that the air alone is capable of oxidizing arsenious oxide when thus heated with lime or soda. Gelstharp found that even sodium sulphate oxidized arsenious oxide when fused with it in a covered crucible, as was shown by the formation of sodium sulphide. He further states that the Pittsburgh plate glass was found by him to retain 56 per cent of the arsenic put in, entirely in the form of arsenate.

Our own results show that in all the glasses tested, both plate and optical glasses, the major part of the arsenic present exists in the pentavalent state but that nevertheless a portion exists in the trivalent state.[3]

[1] Hovestadt, "Jena Glass, etc." Translation by J. D. and A. Everett. Macmillan and Co., New York, **1902,** p. 412.

[2] *Trans. Am. Ceram. Soc.*, **15,** 585 (1913).

[3] See the preceding paper in This Journal.

Role of Arsenic in Glass-Making.—Arsenious oxide is used in glass-making with two distinct purposes. In some cases it is supposed to "whiten" the glass. With this function we are not concerned in this paper.

Arsenious oxide is also used in fining or removing the small bubbles from glass; it causes the glass to "boil," in which operation the small bubbles are apparently swept out by larger ones. Other substances which give off gas at high temperatures are used at times for the same purpose—wood, potatoes, etc. Just what the chemical behavior of arsenic in the fining process may be is little understood. Schott[1] suggests that it may depend on the dissociation of arsenates at high temperature attended by the liberation of oxygen. As Schott has elsewhere expressed the view that glass cannot retain arsenic in the trivalent condition, this dissociation should result in the liberation and loss of arsenious oxide as well as oxygen.

Very accurate methods for the determination of both oxides of arsenic now enable us, with the aid of information from the manufacturers, to compare the condition and quantity of arsenic in the finished glass with that of the batch. In the table is given the history of the arsenic in three American optical glasses made at the factory of the Spencer Lens Company at Hamburg, N. Y. The mixing of the batches was very carefully superintended by Dr. C. N. Fenner of the Geophysical Laboratory, from whom we obtained the samples and the composition of the batches from which the percentages of arsenic in the finished glass could be calculated. The history of each pot is known in detail. The table also contains data on two plate glasses. From the batch of each, both plate and optical glasses, we have calculated the percentage of arsenic (as trioxide) which would be found in the finished glass, on the assumption that no arsenic, boric oxide, or alkali was volatilized in the furnace; in other words, that only moisture, carbon dioxide, and oxygen (from KNO_3) were lost. Losses of boric oxide and alkali would of course raise these figures a trifle, but probably not by an appreciable amount. The percentages are given in the table. The table further contains the quantities

[1] Doelter, "Handbuch der Mineralchemie," Leipzig, **1**, 861 (1912).

of trivalent and pentavalent arsenic which we have found in each of the glasses by methods detailed in the preceding article in THIS JOURNAL. From these figures the loss of arsenic was readily calculated. All the glasses have certainly lost arsenic, though of course it is impossible to say *at what stage* of the process it was lost. The green plate was the only glass of the batch to which niter was not added, and here the loss of arsenic is distinctly larger. With this exception the losses are of a similar order of magnitude. Concerning this loss of arsenic, an observation made by R. L. Frink[1] is of considerable interest. He found, in the bubbles or "seeds" of a glass, crystals which were identified both microscopically and chemically as arsenious oxide. So far as it goes, this observation supports the hypothesis of the dissociation of arsenic pentoxide and the volatilization of arsenic trioxide. Thus it appears that arsenic trioxide is oxidized at low

TABLE.

Showing the condition of arsenic in the finished product and the loss of arsenic in the making of five American glasses.

	Kind of glass.	Taken. As_2O_3. %	Found. As_2O_5. %	Found. As_2O_3. %	Found. Total arsenic cal. as As_2O_3. %	Lost in % of glass.	Lost in % of As_2O_3.
1.	"T" Medium flint containing 42 per cent PbO	0.48	0.38	0.05	0.38	0.10	21
1.	"P" Light flint containing 38 per cent PbO....	0.40	0.35	0.05	0.35	0.05	12
1.	"V" Baryta flint containing 38 per cent PbO and 6 per cent BaO	0.26	0.23	0.03	0.23	0.03	11
2.	Spectacle crown	1.09	0.99	0.08	0.93	0.16	15
2.	Green plate.....	0.36	0.18	0.09	0.24	0.12	33

1. Optical glasses manufactured by the Spencer Lens Co. at Hamburg, N. Y.

2. Optical glasses manufactured by the Pittsburgh Plate Glass Co.

[1] *Trans. Am. Ceram. Soc.*, **17**, 798 (1915).

temperature and the product formed is stable enough to remain until a high temperature is reached and the glass becomes fluid, when it slowly dissociates into oxygen and arsenic trioxide, both of which aid in the fining.

Further consideration of this interesting question must be postponed until we have more data on the behavior of arsenates and arsenites at high temperatures.

The authors wish to express their thanks to the authorities of the Pittsburgh Plate Glass Company and the Spencer Lens Company, and also to Dr. Fenner for the information and material which they very kindly placed at our disposal.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTE OF WASHINGTON,
WASHINGTON, D. C., January 15, 1919.

THE PARTIAL PURIFICATION OF ZIRCONIUM OXIDE.

By A. J. Phillips, Emporium, Pa.

Zirconium oxide is a very desirable refractory for use at high temperatures, its high melting point as well as its low coefficient of expansion causing it to be very satisfactory with respect to checking and spalling upon rapid heating and cooling; likewise its low thermal conductivity renders it very desirable as an insulating material in certain kinds of work.

In the course of some work on spark plug bodies a considerable quantity of the oxide was required for experimental purposes, the specification calling for less than 0.1 per cent of Fe_2O_3. A search was therefore made for a method which would remove the iron oxide alone, the material thus purified and still containing silica, alumina and oxide of titanium being sufficiently pure for the purpose.

The crude zirconia secured from the Foote Mineral Co. of Philadelphia was received already ground to a fineness of 75 per cent through the 100-mesh sieve and recourse was made to the effect of sintering it with various fluxing agents. Sintering with sodium carbonate gave an incompletely decomposed product which on leaching with weak acid filtered very slowly and still contained too much iron oxide to be satisfactory; furthermore the amount of manipulation involved was excessive.

Roasting with ammonium chloride removed very little of the iron as chloride and roasting with sodium chloride to 1500° C gave a product containing considerable amounts of fixed alkali and an iron oxide content of 1.5 per cent. Repeated treatments with sodium chloride did not lower the iron oxide content, while the alkali content increased with each treatment.

A search of the literature showed a large number of methods reported for the decomposition of zircon, a rather complete bibliography being given by J. W. Mellor.[1]

In order to compare several of these methods of decomposition

[1] "Quantitative Inorganic Analysis," Vol. 1, p. 499.

a sample, usually 10 grams, was incorporated with a "decomposer," molded into a small cylinder and fired in a direct flame to 1200–1300° C. After the firing the ignited material was ground, treated with a 10 per cent solution of hydrochloric acid for two hours and filtered. A weighed portion of the residue was then fused with sodium bisulfate and the iron after reduction with hydrogen sulfide, titrated with permanganate. In the following table is given the percentage of iron oxide remaining after several different methods of treatment.

TABLE 1.

Composition.		Per cent Fe_2O_3.
1.....	1 part ZrO_2 + 1 part Na_2SO_4 + $^1/_2$ part C...	1.70
2.....	1 part ZrO_2 + 1 part Na_2SO_4 + 1 part C....	1.79
3.....	1 part ZrO_2 + excess of Na_2S.....	0.88
4.....	1 part ZrO_2 + 1 part NaCl.....	1.68
5.....	1 part ZrO_2 + 1 part NaCl + $^1/_2$ part C....	1.45
6.....	1 part ZrO_2 + 1 part NaFl.....	0.92
7.....	1 part ZrO_2 + 1 part NaFl + $^1/_2$ part C.....	0.79
8.....	1 part ZrO_2 + $^3/_4$ part NaFl + $^1/_4$ part Na_2SO_4	0.91

The use of sodium sulfide as a flux was not as satisfactory as the results appear, since further treatment did not seem to have any effect on the remaining iron oxide. Further work was then done with the fluorides as they had the best effect, although two well-known methods of fluoride decomposition were not tried; one using a mixture of sodium hydrate and sodium fluoride, the other acid potassium fluoride, as both methods would involve the use of containers on account of the fluxing of the mixture.

A consideration limiting the use of various reagents was found in the amount of zirconia rendered soluble by leaching with hydrochloric acid in each case. In all of the treatments the leachings were reduced with hydrogen sulfide and boiled with a solution of sodium thiosulfate, in order to precipitate the hydroxides of zirconium, titanium and aluminium. It was necessary to reduce first with hydrogen sulfide, since before the liberated sulfur dioxide reduced the iron to the ferrous condition, the precipitate formed absorbed or occluded ferric iron which was not subsequently reduced and removed by the sulfur dioxide—even after the reduction the precipitated material was not entirely free from iron

oxide. It was therefore thought important to weigh the residues in each case after the acid treatment and ignition, in order to determine how much was rendered soluble and would require further treatment.

TABLE 2.

	Composition.	Per cent residue.	Per cent Fe_2O_3.
1.....	1 part ZrO_2 + $^1/_2$ part $KBFl_4$.....	58.29	0.70
2.....	1 part ZrO_2 + $^1/_2$ part ($^1/_2$ NaFl + $^1/_2$ $Na_2S_2O_7$)..	73.53	0.85
3.....	1 part ZrO_2 + $^1/_2$ part ($^3/_4$ NaFl + $^1/_4$ C).....	66.62	0.79
4.....	1 part ZrO_2 + $^1/_2$ part ($^3/_4$ $Na_2S_2O_7$ + $^1/_4$ C).....	81.00	0.96
5.....	1 part ZrO_2 + $^1/_2$ pt. (2.5 pts. $CaFl_2$ + 1 pt. H_3BO_3)	64.40	1.21
6.....	1 part ZrO_2 + $^1/_2$ part (5 $CaFl_2$ + 1 $Na_2B_4O_7$)....	52.62	1.15
7.....	1 part ZrO_2 + $^1/_2$ part (5 NaFl + 1 $Na_2B_4O_7$).....	63.40	0.62
8.....	1 part ZrO_2 + $^1/_2$ part ($^1/_2$ $Na_2S_2O_7$ + $^1/_2$ $Na_2B_4O_7$)	61.20	0.69

Table 2 shows the composition of the material ignited; the percentage of material remaining after igniting, leaching with acid and again igniting; and the percentage of iron oxide remaining after the treatment.

The first mixture fused and it was necessary to run it over in platinum; the others were brittle and pulverized readily. All of the mixtures containing sodium pyrosulfate filtered poorly—due to the presence of much gelatinous material. In general the sodium fluoride-borax mixture was the best, but even its behavior was not entirely satisfactory as evidenced by the presence of 0.62 per cent residual iron oxide. In cases where calcined zirconia is ground and dissolved in hydrofluoric acid in order to effect subsequent precipitation as potassium zirconium fluoride, the use of this mixture would be advantageous since no container is required for the fusion, whereas, when an acid fluoride is used, a graphite or carborundum crucible is necessary.

The possibilities of acid treatment alone were then considered, since Wedekind[1] has recommended continued digestion with this acid and Rosenhain[2] states that the impure material readily stands a temperature of 1600° C while the refractory qualities are much improved by digestion with hydrochloric acid to remove a part of the iron oxide.

[1] *Berichte*, **43**, 290–7 (1910).
[2] *Met. Chem. Eng.*, **15**, 674 (1916).

For the acid tests, 10 grams of powder, which passed the 100-mesh sieve, were digested with 50 cc. of acid for three hours on a steam plate at 100° C and the iron oxide in the residue determined. In addition the effect of a small amount of pressure or at least the prevention of the volatilization of the acid was effected by placing the powder and acid in a small bottle with a spring cover and heating it in boiling water. In two cases the acid was first saturated with chlorine gas. The results were as follows:

	Compositions.	Per cent Fe_2O_3 in residue.
1.....	10 grams powder, 50 cc. HCl.....	1.52
2.....	10 grams powder, 50 cc. HCl in bottle.....	1.40
3.....	10 grams powder, 50 cc. HCl sat. with Cl.....	1.48
4.....	10 grams powder, 50 cc. HCl in bottle sat. with Cl....	1.34

A few other tests were made involving the use of HCl; in one of them the zirconia was acid-treated after having been heated to 900° C for three hours in a current of hydrogen. The results were not satisfactory. In another case dry hydrochloric acid gas was used instead of hydrogen and while the iron oxide not removed by digestion with acid was reduced to 0.62 per cent, yet this was considered still too high.

Chlorine gas was then tried on a small scale by passing it over the ore in an electrically heated tube. The results were so encouraging that a gas-heated furnace was built in which the ore was heated in an upright cylindrical muffle, while chlorine was introduced at the bottom through a piece of glazed pyrometer tubing.

The simultaneous use of chlorine and carbon as explained by Thomsen[1] causes a great reduction of the temperature at which the iron oxide is decomposed. In the succeeding work, therefore, the crude zirconia was mixed with about 4 per cent of finely powdered petroleum coke, molded into small balls and heated in the muffle in an atmosphere of chlorine to 900° C.

The question of retorts in which to conduct the chlorination is an important one and probably a dense, completely vitrified material resembling chemical stoneware would be most satisfactory. The cylinders first used were jiggered from a mixture

[1] "Thermochemistry," p. 357.

of 55 per cent grog passing an 8-mesh but retained on a 30-mesh sieve, 35 per cent Florida kaolin and 10 per cent Tennessee ball clay. While withstanding the rapid heating and cooling employed, they were entirely too porous, the chlorine penetrating and coming through the walls as shown by their whitening. A better mixture was later secured, it being a glass-pot mixture of Laclede Christy bond clay, Illinois and Newark kaolins, Arkansas and Highlands fireclays with 60 per cent of 12-mesh grog composed of North Carolina kaolin and calcined Highlands fireclay. This cylinder became red with repeated use, showing the penetration of iron oxide, and apparently grew denser with time. Porcelain jars were tried but cracked with rapid temperature changes and porcelain inlet tubes for the chlorine became very porous even though not heated to any extent.

To further increase the density of the cylinders they were painted with a mixture of sodium silicate and clay which on heating fused to a smooth glaze. On the external surface the glaze coating was slowly volatilized, but on the inner surface a dense, white salt coating was formed which did not spall to any appreciable extent.

It was soon found that zirconium chloride was being volatilized out of the furnace along with the iron chloride, for on dissolving some of the sublimate in dilute HCl, neutralizing, saturating with SO_2 and boiling the solution, a considerable precipitate of hydrated zirconia was secured.

Prescott and Johnson,[1] state that zirconia with charcoal is volatilized as the chloride in a current of chlorine.

In order to recover this material a cylindrical reverberatory type of furnace was built with a long cooling chamber. It was also thought that passing the products of combustion over the material would maintain a reducing atmosphere which might result in cutting down the amount of carbon required in the raw mix. However, the fact that the chlorine sank to the bottom of the cylinder and was swept out by the current of gases kept the balls at the top from being properly chlorinated unless a large excess was used; therefore a return was made to vertical chlorination, an up-draft furnace being used and the products of com-

[1] "Qualitative Chemical Analysis," p. 203.

bustion passed through the mix. The construction of the furnace is shown in Fig. 1.

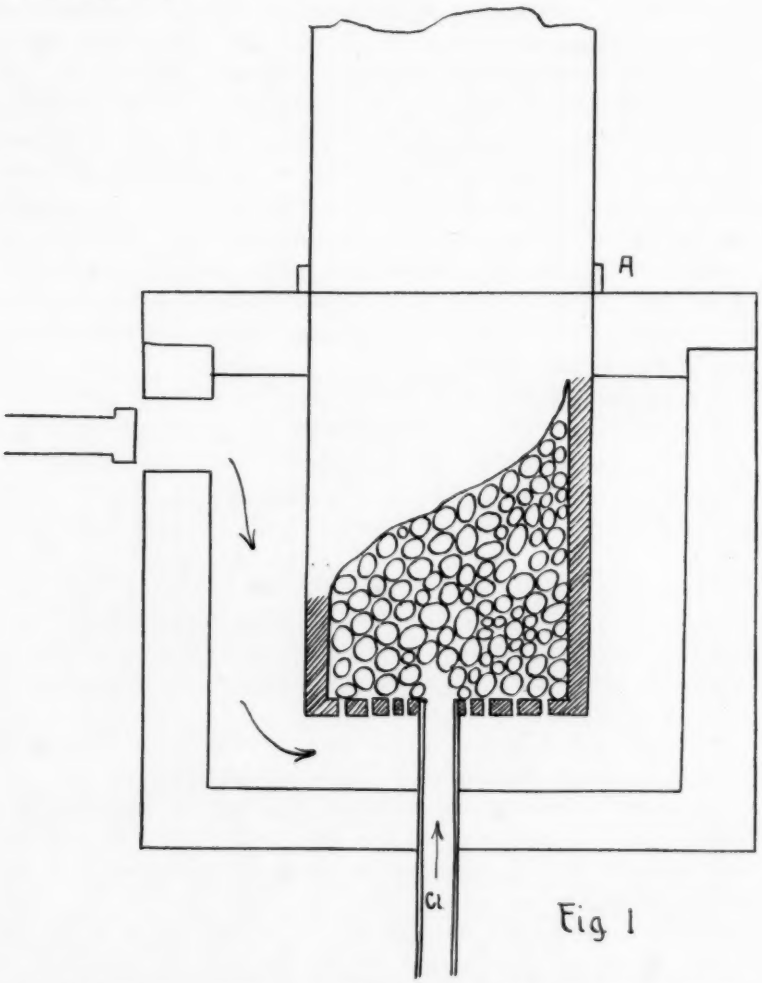


Fig. 1

With this furnace the top was closed and the gas and air introduced near the top, the draft being upward through holes in the bottom of the cylinder. Owing to the limited space, combustion was very imperfect and it was necessary to keep the tip of the

burner partly outside of the furnace. The result of this partial combustion was that a considerable quantity of water vapor was formed and condensed at the joint A, so that the clay luting around the joint was dripping wet during over half the run, and water vapor with HCl gas issued from the stack throughout the run. The effluent contained considerable iron oxide as shown by its red color as it dried on the outside; however, an examination of the material showed that little or no zirconia was present and it was suggested that external heating be used and that the chlorine be passed through water. This was finally the method adopted, the chlorine being passed through a bubble tube near the furnace. Cold water was not nearly so efficient as hot water in the bubble tube in retarding the choking of the apparatus with volatilized iron chloride and probably for larger installations the injection of low pressure steam along with the chlorine would be most satisfactory.

In chlorinating with external heating and exposure of the material to the air at the top of the furnace, peculiar incrustations like "Pharaoh's serpents" collected over the top layer, whereas, in cases where up-draft and a stack were used, the sublimate was deposited as a fine powder upon the walls—the color in most cases being an indication of how much zirconia had been volatilized along with the iron oxide.

An interesting fact was that apparently the size of the specimens made no difference, as balls from $^1/_4$ in. to 1 in. diam. were chlorinated at the same rate and the necessity for the fine grinding usually specified in decomposing this material was entirely obviated—the raw material with only 75 per cent passing the 100-mesh sieve being successively used.

The penetration of the chlorine was shown by the fact that in every case where a ball was white on the outside, it would also be white on the inside right to the core. In a few cases some of the balls at the top of the cylinder were white on the inside and yellow or coated with yellow crystals on the outside. This was evidently caused by iron chloride being volatilized lower down in the hotter part of the furnace and being deposited on the cooler material near the top.

The question then arose as to whether or not it would be possible to chlorinate the material without first mixing with a binder and molding into balls. Very probably, however, this would be possible only if a rotating drum were used since there is always some iron chloride which collects at the top layer of material and which would sooner or later choke the furnace and shut off the flow of chlorine.

It would be possible then to press the crude zirconia into bricks with a little binder, pile them in checker work in a furnace and chlorinate them in place—if it were not for the fact that chlorination removes the iron oxide bond in the material and after chlorination it is very mealy, porous or punky. The oxide being heavy, the bricks would then fall to pieces or at least crush those at the bottom of the pile. Even by firing to cone 35, which was done in some cases in calcining the finished material, a very slight bond was developed, the specimens being porous and not permitting much handling.

In order to secure more quantitative figures as to the loss of zirconia, two samples were chlorinated in an electrical tube-furnace under the same conditions except that in one case the chlorine was passed through cold and in the other, boiling water. The analyses as given below show (1) for cold and (2) for boiling water.

	1. Per cent.	2. Per cent.
SiO_2	15.52	11.49
Al_2O_3	2.44	1.87
Fe_2O_3	0.04	0.03
CaO	0.68	0.49
P_2O_5	0.05	0.03
Na_2O	0.06	0.05
K_2O	0.09	0.08
ZrO_2	80.91	85.93
TiO_2	0.18	0.16

If we take the following analysis (3) of the raw material and calculate out the ignition loss and the oxides removed by wet chlorine, *viz.*, Fe_2O_3, MnO_2, P_2O_5, and TiO_2, we obtain a theoretical composition as shown in (4):

	3. Per cent.	4. Per cent.
SiO_2	10.62	11.56
Al_2O_3	1.71	1.86
Fe_2O_3	2.90	....
CaO	0.42	0.45
P_2O_5	0.65	....
Na_2O	0.04	0.04
K_2O	0.06	0.06
ZrO_2	79.25	86.31
TiO_2	1.81	....
Ig Loss	2.78	....

By comparing analysis 4 with 1, about 5 per cent, and with 2, less than 0.5 per cent ZrO_2 was lost in chlorination.

In explaining the course of the reactions, we might suppose that the chlorides of iron and zirconium would be formed and volatilized at the same rate with a loss of zirconium chloride at least equal to that of the iron chloride. However, Mellor[1] states that if a certain resistance is to be overcome before a reaction can be started, the process which requires the least energy for its initiation will be produced in preference; furthermore, if the two reactions have actually started side by side, the relative velocities of the two reactions will determine which one takes place to the greatest extent. Iron chloride volatilizes at 100° C while the zirconium chloride volatilizes at or about 400° C; so it is probable that there is a preferential formation and volatilization of the iron chloride. As the temperature is gradually raised we have the establishment of a reversible reaction, $FeCl_3 \rightleftharpoons FeCl_2 + Cl$, or, according to Burgess,[2] two independent components form the system which is divided into three phases, $FeCl_3$, $FeCl_2$ and Cl. The system is therefore mono-varient and admits a curve of dissociation temperatures. Therefore at any temperature T, equilibrium corresponds to a tension P of the chlorine atmosphere which is determined by a knowledge of the temperature T. If the rate of chlorine introduction is increased so that the pressure becomes greater than P, the $FeCl_2$ again absorbs Cl until the pressure equals P and if the chlorine is reduced, $FeCl_2$ is reduced

[1] "Chemical Statics and Dynamics," p. 325–6.

[2] "Thermodynamics and Chemistry," p. 155.

until the pressure takes its former value. In other words, an equilibrium is constantly tending to be formed.

Now with the introduction of water vapor the equilibrium is disturbed; there is a partial decomposition of the vapor into hydrogen and oxygen which reacting with the chloride tends to the formation of a new equilibrium containing among some other products, oxide of iron and hydrochloric acid gas. If we apply the same considerations to the zirconium chloride we shall establish a system containing some zirconia and hydrochloric acid gas. There would thus be no advantage in the introduction of water vapor if it were not for the fact that iron oxide mixed with carbon is volatilized as the chloride in a current of hydrochloric acid gas while zirconia is not affected thus; so that as we have an excess of carbon present the conditions are favorable for the removal of the iron oxide alone.

Thus as the action to a large extent depends on hydrochloric acid gas, it might seem advantageous to use it throughout in decomposing the material, but in the tests made the decomposing action of the hydrochloric acid gas was not sufficient to remove the last 0.5 per cent of iron oxide, the more energetic chlorine being required to break up the combination in which the iron oxide exists in the crude zirconia.

It is obvious that the treatment is applicable not only to the purification of crude zirconia, but also to bauxite and flint for the removal of iron oxide.

In conclusion we beg to acknowledge our indebtedness to Mr. A. V. Bleininger of the Bureau of Standards, for suggestions and assistance in outlining the work.

STRENGTH TESTS OF PLAIN AND PROTECTIVE SHEET GLASS.[1]

By T. L. Sorey, Washington, D. C.

This paper deals with strength tests of plain sheet glass and one type and make of protective glass. The protective glass, which will be designated as Type A, consists of sheet glass to one side of which is firmly attached a thin sheet of celluloid. The intention is that the glass shall be used with the celluloid or treated side toward the person to be protected. This is one of several kinds of protective glass which are to be investigated and therefore at present no statement can be made as to the value of this glass compared with other protective types. However, the effect of the thin coating of celluloid on the mechanical properties of the glass is interesting, and the presence of this coating enables us to study the manner in which sheet glass is fractured by various forces.

The samples were subjected to firing tests, impact tests and cross bend tests as follows:

Firing Tests.

The sheets of glass used for this test were 8″ by 10″ and of three thicknesses, $1/8$″, $3/16$″, and $1/4$″. The $1/8$″ and $1/4$″ thicknesses were plate glass while the $3/16$″ thickness was tested in both a plate and a special blown window glass. One lot of glass of each thickness was plain and another was Type A protective glass.

The samples were clamped firmly to a board frame with bearings on rubber strips $3/16$″ thick. One set of bearing strips was near the edges of the glass and another around a rectangular hole, $2\,1/2$″ by 5″, at the center of the sheet. The samples were then perforated by bullets fired from a regulation army rifle at a distance of fifty feet.

The following observations were made from the results of the firing tests:

[1] By permission of the Director, Bureau of Standards.

A. Plain glass:

All samples were completely broken and shattered.

B. Type A protective glass:

1. The glass remained in place with the exception of a small area, in the immediate vicinity of the point of entrance, which was pulverized and carried through with the bullet.

2. The thinner the sheet the fewer the cracks.

3. A smaller hole and fewer cracks resulted when the bullet entered perpendicularly to the surface than when it entered at an angle of 45°.

4. Fewer cracks resulted when the bullet entered from the treated side.

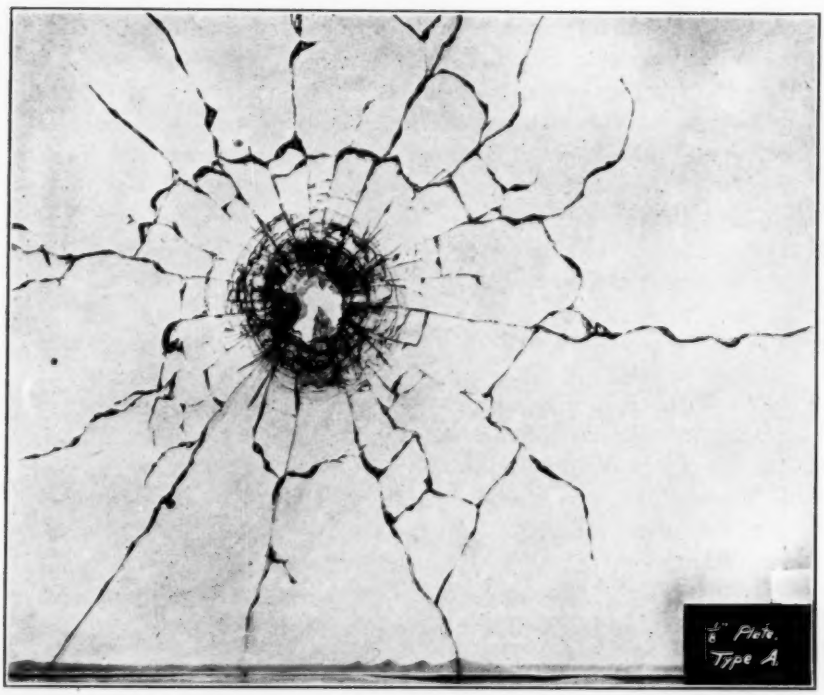


FIG. 1.

5. The effect of the shock was less on blown window glass than on plate glass of the same thickness.

6. When the cracking was the most extended as in a few of the thickest samples, the plate bent at the middle but was held together by the celluloid.

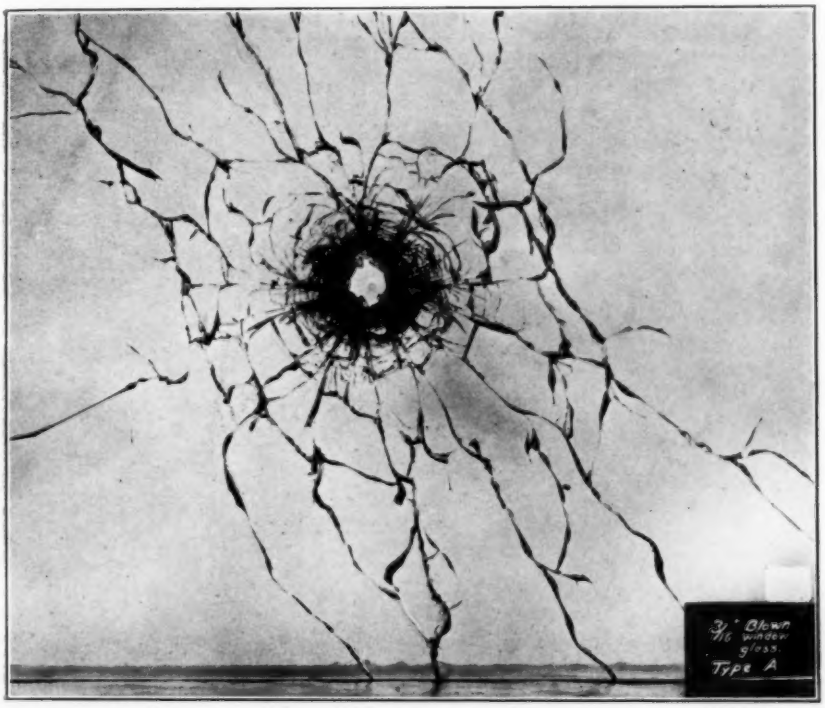


FIG. 2.

7. In handling and cleaning the samples, the celluloid was easily scratched or marred if there was any grit on the surface.

The effects of bullets fired perpendicular to the surfaces and against the uncoated sides of the Type A samples are shown in Figs. 1 to 4. These are typical fractures.

Impact Tests.

The samples used in this test were of the same size and kinds as those used in the firing tests, except that no $^3/_{16}''$ plate glass was tested. The specimens were placed in the frame used in the firing tests and this was supported solidly on the steel frame of an impact testing machine of the pendulum type. The pendulum

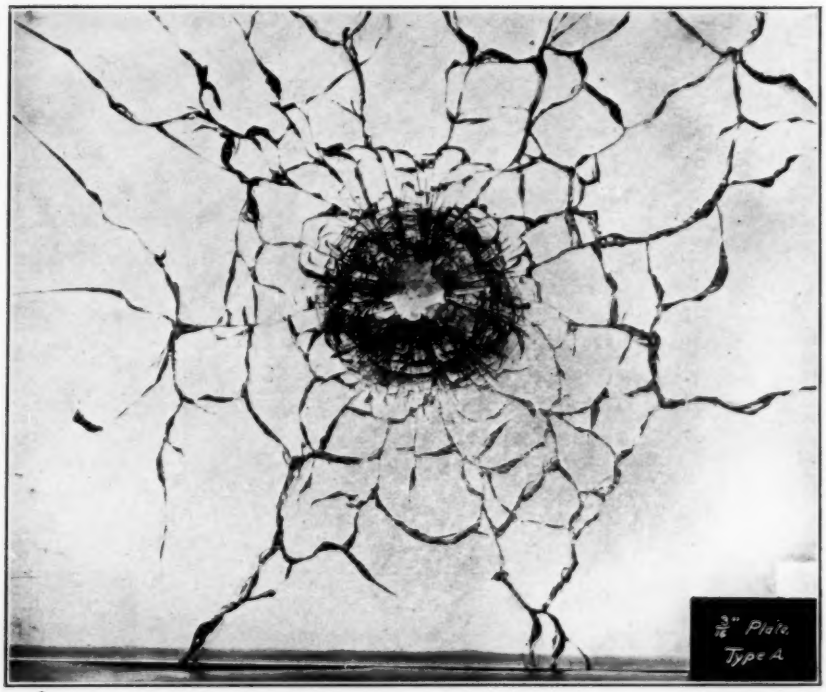


FIG. 3.

consisted of a $1^1/_4$ pound flattened steel ball at the end of a 24″ stiff wire arm. The hammer had a spherical striking surface with a radius of $1^1/_8''$.

In making these tests the pendulum was first allowed to swing through 5°, then 10°, and so on, the angle of swing being increased each time by 5° until fracture occurred. However, a

fall through 90° was not sufficient to break some of the specimens, in which cases the hammer was dropped repeatedly through 90° until the piece was fractured. The angle or the number of repetitions at 90° was recorded. On several of the samples of protective glass the test was continued until there was complete fracture of both glass and celluloid.

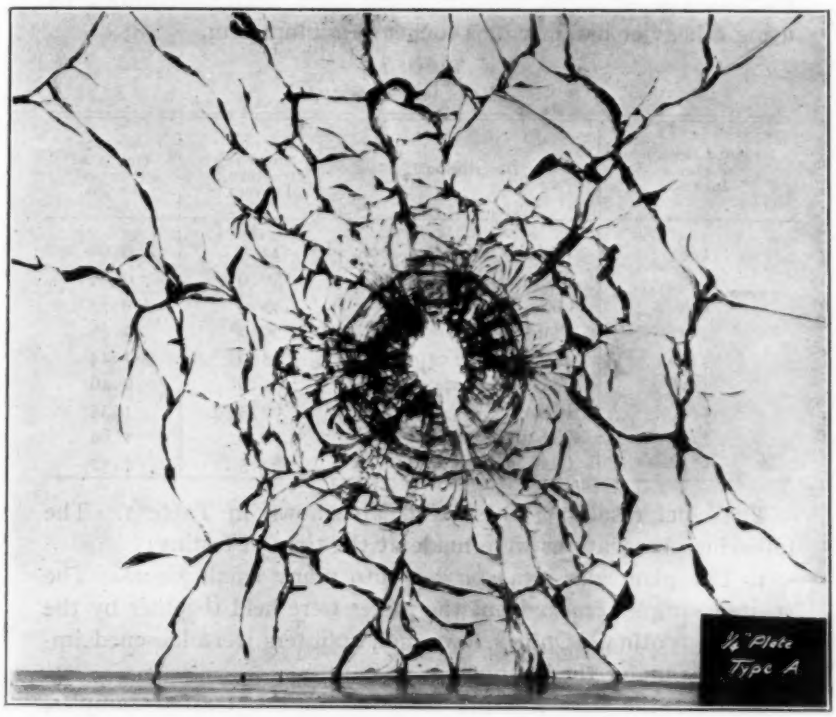


FIG. 4.

The energy of impact in foot pounds of a swinging pendulum, when impact occurs as in this case perpendicularly below the point of suspension, is calculated by the use of the following formula:

$$E = 1 - \text{cosine angle A} \times L \times W,$$

in which

Angle A = angle with vertical made by the pendulum arm at the time of release.

L = length of arm in feet.
W = weight of hammer in pounds.

It is impossible to figure the effect of repetitions of the same blow or blows of increasing severity—due to lack of data on the mechanical properties of glass. If the time required to alter the apparatus had been available, the energy of impact necessary to fracture the strongest samples could have been determined by using a heavier hammer or a longer pendulum arm.

TABLE 1.
Results of impact tests.[1]

Nominal thickness of glass. Inches.	Description.	Average angle at fracture. Degrees.	Average energy at fracture. Ft. lbs.
1/8	Plain	42.5	0.66
1/8	Treated side exposed	50.0	0.89
1/8	Glass side exposed	45.0	0.73
3/16	Plain	90.0[2]	2.46
3/16	Treated side exposed	65.0	1.44
3/16	Glass side exposed	90.0[3]	2.46
1/4	Plain	62.5	1.35
1/4	Treated side exposed	70.0	1.64
1/4	Glass side exposed	82.5	2.17

The chief results of these tests are shown in Table 1. The following observations were made at the time of testing:

1. The plain glass was broken into many small pieces. The treated samples cracked but the pieces were held together by the celluloid coating. Only a few small splinters were loosened immediately under the hammer.

2. After the first fracture occurred in the treated samples, only two or three more blows were required to break the celluloid and splinter the glass.

3. The cracked area was smaller on the thinner samples.

4. Fewer but more extended cracks were caused when the blow fell on the treated side than on the glass side.

[1] Each of the values given in the table is the average of two tests.

[2] One sample did not break with 170 repetitions at 90°.

[3] Repeated an average of 8 times. Energy of impact figured simply as of 90°.

Attention may be called to the fact, as shown in Table 1, that the $^3/_{16}''$ uncoated blown window glass was stronger than the $^1/_4''$ plate glass. Also, that the amount of energy required to cause the first crack in the glass was not materially increased by the celluloid coating.

Cross Bend Tests.

The samples used were 2″ by 12″ and of three thicknesses, as in the preceding tests. The $^1/_8''$ and $^1/_4''$ thicknesses were plate glass and the $^3/_{16}''$ thickness was blown window glass.

In making the tests, two wooden bearing blocks of triangular section were placed on the platform of a small counter scales so as to give a span of 10 inches. A strip of glass was laid on these and the load applied to the middle of the sample by means of a rod screwed downward through a steel yoke placed above the scales The lower end of the rod was provided with a bearing block of semi-circular cross-section resting in a ball and socket joint. Thin bearing strips of rubber were interposed between the glass and the three blocks.

TABLE 2.

Results of cross bend tests.[1]

Nominal thickness. Inches.	Description.	Actual average thickness. Inches.	Average load at failure. Pounds.
1/8	Plain	0.142	20.5
1/8	Treated side up	0.145	17.5
1/8	Treated side down	0.152	31.5
3/16	Plain	0.175	36.0
3/16	Treated side up	0.186	25.0
3/16	Treated side down	0.190	46.5
1/4	Plain	0.229	44.5
1/4	Treated side up	0.241	38.5
1/4	Treated side down	0.242	60.0

The results of these tests are shown in Table 2. Fracture occurred under the point of application of the load and was generally in the form of a V-shaped group of cracks.

[1] Each of the values given in this table is the average of two tests.

A study of Table 2 shows that the treated samples of a given kind and thickness were about 15 per cent weaker than the plain glass when the celluloid side was in compression and about 40 per cent stronger when the celluloid side was in tension.

Summary.

The following recapitulation may be made of the salient points of these tests:

1. It is possible to determine some of the physical properties of sheet glass in a fairly accurate manner by the use of a comparatively simple testing apparatus.

2. In both the impact and cross bend tests, the blown window glass was stronger than the plate glass.

3. While the energy of impact necessary to produce fracture increased with the thickness of the plate glass, the amount of cracking occurring at the time of initial fracture also increased.

4. The force of the blow required to crack a piece of glass of a given kind and thickness was not materially increased by the celluloid coating, but the shattered glass remained in place while the plain glass was scattered.

5. In the cross bend tests the treated glass of a given kind and thickness was about 15 per cent weaker than the plain glass when the celluloid coated side was in compression and about 40 per cent stronger when the celluloid coated side was in tension.

ERRATA SLIP

"Some Phenomena in Glaze Reduction," by H. B. Henderson, Vol. 1, No. 3, page 148 *et seq.*

Page 149 line 4 from the top omit the word "somewhat."

Page 149 line 12 from the bottom change the word "graphitic" to "graphite."

Page 151 line 14 from the top omit the words "iron oxide."

Page 151 line 19 from the top insert the words "some of" after the word "glaze."

Page 152 line 12 from the top insert the word "ferrous" before the word "iron."

Page 152 change the footnote to read: "Sosman and Hostetter, *Trans. American Inst. Mining Engineers, Bull.* **126.**"

Page 153 line 4 from the top change "will" to "may."

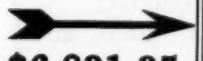
Page 153 line 23 from the top change "color" to "coloring matter."

Page 155 lines 11 and 12 omit the clause "except by the assumption of transformation and diffusion effects."

Page 155 line 15 from the top change "but" to "and."

Page 155 line 17 from the top change "probable" to "evident."

Page 155 line 19 from the top insert the clause "if it is iron" after the word "iron."



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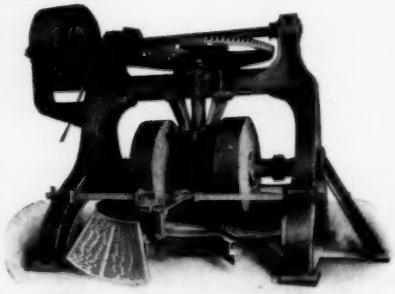

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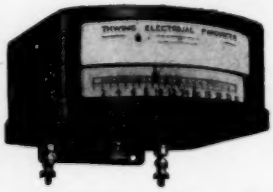

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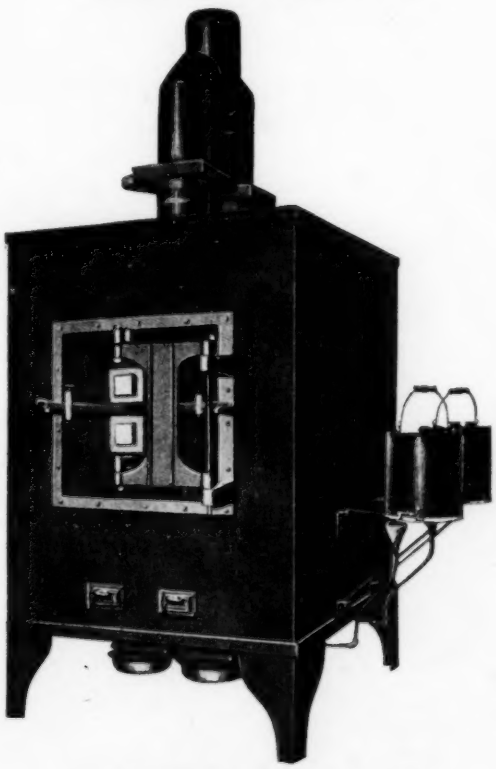

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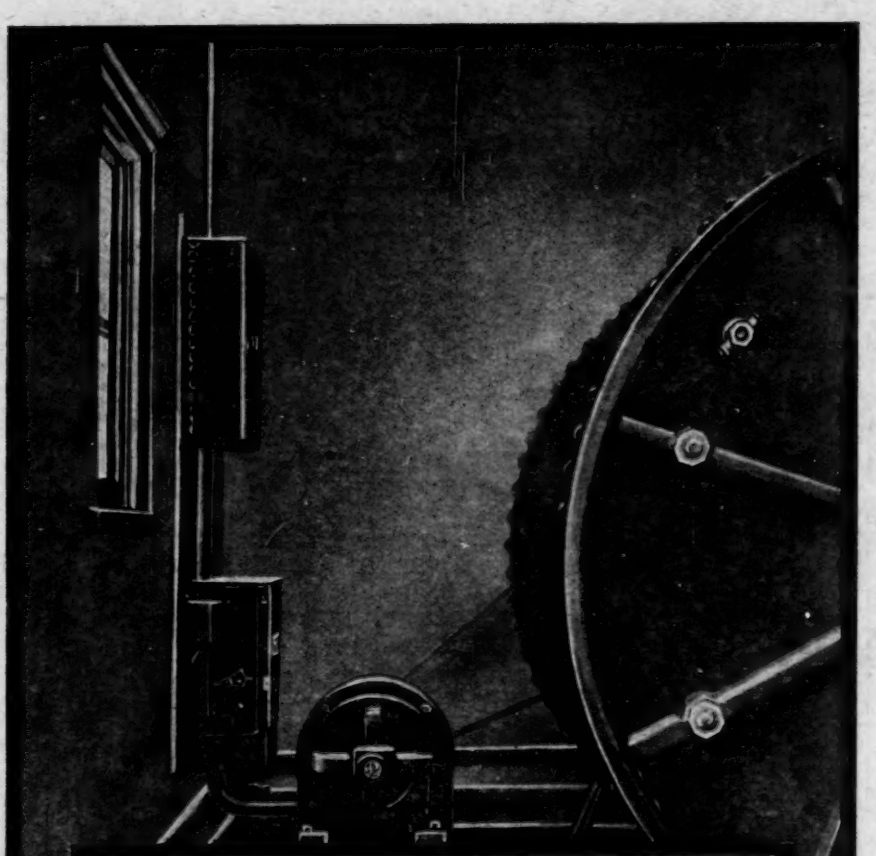
THE HARSHAW FULLER AND GOODWIN CO.

CLEVELAND NEW YORK PHILADELPHIA



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G-E Individual Motor Drive saves many dollars formerly spent for upkeep of line shafts, hangers, pulleys and belts.

It is safer—cleaner—permits of better use of floor space, eliminates shadows from belts, which mean better light.

It saves power, consequently money, as the power consumption is proportional to work done. You can operate any individual machine and not have to have the whole power system in operation.

There is a certainty, smoothness and sustained speed meaning immediate dollars saved — less wastage — greater safety to operatives.

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